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Volume II. Utility and Large Industrial Boilers

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16. ABSTRACT The proceedings document the 50 presentations made during the Second Stationary Source Combustion Symposium held in New Orleans, LA, August 29-September 1, 1977. Sponsored by the Combustion Research Branch of EPA's Industrial Environmental Research Laboratory--RTP, the symposium dealt with subjects relating both to developing improved combustion technology for the reduction of air pollutant emissions from stationary sources, and to improving equipment efficiency. The symposium was divided into six parts, and the proceedings were issued in five volumes: Volume I--Small Industrial, Commercial, and Residential Systems; Volume II--Utility and Large Industrial Boilers; Volume III--Stationary Engine, Industrial Process Combustion Systems, and Advanced Processes; Volume IV--Fundamental Combustion Research; and Volume V--Addendum. The symposium was intended to provide contractor, industrial, and Government representatives with the latest information on EPA inhouse and contract combustion research projects related to pollution control, with emphasis on reducing nitrogen oxides while controlling other emissions and improving efficiency.

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PROCEEDINGS OF THE SECOND STATIONARY SOURCE COMBUSTION SYMPOSIUM

Volume II. Utility and Large Industrial Boilers

Symposium Chairman Joshua S. Bowen
Vice-Chairman Robert E. Hall

Environmental Protection Agency
Office of Research and Development
Industrial Environmental Research Laboratory
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PREFACE

These proceedings document the more than 50 presentations and discussions of the Second Symposium on Stationary Source Combustion held August 29 - September 1, 1977, at the Marriott Hotel in New Orleans, Louisiana. Sponsored by the Combustion Research Branch of the EPA's Industrial Environmental Research Laboratory-Research Triangle Park, the symposium presented the results of recent research in the areas of combustion processes, fuel properties, burner and furnace design, combustion modification, and emission control technology.

Dr. Joshua S. Bowen, Chief, Combustion Research Branch, was Symposium Chairman; Robert E. Hall, Combustion Research Branch, was Symposium Vice-Chairman and Project Officer. The Welcoming Address was delivered by Dr. John K. Burchard, Director of IERL-RTP; the Opening Address was delivered by Robert P. Hangebrauck, Director, Energy Assessment and Control Division, IERL-RTP; and Dr. Howard B. Mason, Program Manager NO_x Environmental Assessment Program, Acurex Corporation, delivered the Keynote Paper.

The symposium consisted of six sessions:

Session I: **Small Industrial, Commercial and Residential Systems**
Robert E. Hall, Session Chairman

Session II: **Utility and Large Industrial Boilers**
David G. Lachapelle, Session Chairman

Session III: **Special Topics**
David G. Lachapelle, Session Chairman

Session IV: **Stationary Engine and Industrial Process Combustion Systems**
John H. Wasser, Session Chairman

Session V: **Advanced Processes**
G. Blair Martin, Session Chairman

Session VI: **Fundamental Combustion Research**
W. Steven Lanier, Session Chairman

VOLUME II

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SESSION II:

UTILITY AND LARGE INDUSTRIAL BOILERS

DAVID G. LACHAPELLE
CHAIRMAN

FIELD TESTING: APPLICATION OF COMBUSTION MODIFICATION TO POWER GENERATING COMBUSTION SOURCES

By:

A. R. Crawford, E. H. Manny, and W. Bartok
Exxon Research and Engineering Company
Linden, NJ 07036

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ABSTRACT

A field study program was conducted to assess the applicability of combustion modification techniques to the control of NO_x and other pollutant emissions from power generating combustion sources. This work is part of a continuing series of field test programs performed by ER&E on utility boilers and other power generating combustion sources. The goal of this research is to determine whether known modifications can be applied to the combustion process for NO_x control, without causing deleterious side effects.

The studies reported in this paper include field tests on utility boilers and gas turbines employed for power generation. Comprehensive, statistically designed test programs were conducted to evaluate the effect of combustion modifications on NO_x and other gaseous emissions. In addition, particulate mass and size distribution and boiler efficiency were determined under baseline and low NO_x operating conditions.

The most extensively studied combustion modification for utility boiler applications was staged firing at low excess air. This approach can achieve reductions in NO_x emissions up to about 50% based on the results of short term tests. With the focus of the program on NO_x emission control for coal fired utility boilers, special attention was paid to the determination of potentially adverse side effects--increased combustible emissions, unwanted changes in particulate mass loading and size distribution, reduced boiler efficiency, increased waterwall slagging and external corrosion, and flame problems.

Short term tests indicate that staged combustion may be applied to coal fired utility boilers. The extent of waterwall corrosion and slagging could not be determined unequivocally based on the results of 300-hour corrosion probing runs under low NO_x and baseline operating conditions. For this reason, a long term waterwall corrosion test of at least six month duration was initiated at Gulf Power Company's Crist station on a 500 MWe front wall fired boiler. This program is conducted jointly with Foster Wheeler, the boiler manufacturer. In addition to corrosion probing, ultrasonic mapping of the waterwall tube thicknesses is carried out at the beginning and end of the baseline and low NO_x operating periods, and measurements are made on specially installed waterwall test panels to determine the rate of corrosion under staged firing with portions of the furnace operated under fuel rich, reducing conditions.

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ACKNOWLEDGMENTS

The research described in this paper was performed under the sponsorship of the U. S. Environmental Protection Agency, pursuant to Contract No. 68-02-1415. The field testing studies on the Mercer Station Boiler No. 1 of Public Service Electric and Gas Company was funded in part by the Electric Power Research Institute (RP 200). The authors wish to acknowledge the constructive involvement and comments of Mr. R. E. Hall, the EPA Project Officer. Thanks are due to Professor John Tukey of Princeton University for his advice on statistical test design. The cooperation of equipment manufacturers, General Electric Company, Foster Wheeler, Babcock and Wilcox, and Combustion Engineering in selecting representative units is highly appreciated. Special thanks are due to Mr. J. Vaisky of Foster Wheeler for their effective participation in the long term corrosion test program on the Crist Boiler No. 7 of Gulf Power Company, which is being carried out under a subcontract to Foster Wheeler. The voluntary participation of the power generation combustion equipment operators (Public Service Electric and Gas Company of New Jersey, Houston Lighting and Power Company, Gulf Power Company, East Kentucky Power Cooperative, and Colorado Public Service Company) in making available their boilers and gas turbines for testing is gratefully acknowledged. Finally, thanks are due to Messrs. L. W. Blanken, J. F. Bond, J. J. Eggert, W. Petuchovas, R. W. Schroeder, and Mrs. M. V. Thompson for their assistance in performing these studies.

SECTION I

INTRODUCTION

Exxon Research and Engineering Company has been conducting field studies under EPA sponsorship (and in part supported by the Electric Power Research Institute) on the application of combustion modification techniques to the control of pollutant emissions from utility boilers. The emphasis in these studies has been on controlling NO_x emissions without adverse side effects, such as increases in other pollutant emissions, and equipment safety and operability problems.

Because of the difficulty of controlling NO_x emissions from coal fired boilers, the emphasis in the Exxon Research field studies has been on coal fired units. Using a mobile sampling-analytical system designed and built for the first Exxon Research field studies conducted under EPA sponsorship [1] on gas, oil, and coal fired utility boilers, gaseous emission measurements have been obtained on a large number of coal fired utility boilers [2,3]. This comprehensive program includes the measurement of not only gaseous species under baseline and modified combustion conditions, but also particulate mass loading and size distribution measurements. This characterization work is being extended to potentially hazardous inorganic and organic trace constituents of combustion gases.

Reflecting the major remaining question that interferes with the application of combustion modifications (staged combustion) to coal fired utility boilers for NO_x emission control, an extensive effort has been mounted to resolve whether external furnace tube corrosion is accelerated by staged firing of high sulfur coals.

Earlier short term measurements in the Exxon field studies using corrosion probes could not produce an unequivocal answer to this problem. Therefore, a long term corrosion test program was initiated in 1976 on Crist boiler No. 7 of Gulf Power Company in cooperation with that utility and the manufacturer of the unit, Foster Wheeler Energy Corporation, as Exxon Research's subcontractor.

A status report will be presented on the emission tests performed during the current phase of this program and on the long term corrosion tests at Gulf Power's Crist Station.

SECTION 3

GASEOUS EMISSIONS

3.1 Mercer Station, Boiler No. 1
Public Service Electric and Gas Company (New Jersey)

Mercer Unit No. 1 is a twin furnace, front-wall fired, wet-bottom Foster Wheeler boiler. This unit was selected for testing because of its flexibility for combustion modification, and to determine the side-effects of such modifications on a wet-bottom unit. The boiler has 1579 m^2 (16,926 ft^2) of furnace heating surface, a furnace volume of 5111 m^3 (180,332 cubic feet), with each furnace measuring 11.95 m (39 feet 2-1/2 inches) in width and 7.99 m (26 feet 2-1/2 inches) in depth. Maximum continuous rated steam flow is 934.6 t/hr. (2,060,000 lb/hr) at 16.7 MPa (2400 psig) pressure and 867 K (1100°F) superheat steam temperature and 839 K (1050°F) reheat steam temperature. Three ball-type pulverizers feed the 24 burners arranged in three rows of four burners in each of the two twin furnace front walls. The pressurized furnaces are equipped with flat floors and slag-taps.

Analysis of these test results indicate that all of the operating variables included in the experimental program had a significant effect on NO_x emission levels. As shown in Figure 1, at full load (290 MWe), baseline operation resulted in 739 ng/J (1381 ppm) NO_x emissions. This high NO_x level is caused by the unusual furnace design of this boiler in which pulverized coal can be burned at low loads with a wet bottom furnace. The flat furnace floor is relatively close to the bottom row of burners so that unusually high gas temperatures are maintained in the bottom of the furnace in order to maintain the slag in a molten state. Within the limited operating flexibility under full load operation, firing with low excess air was the most important variable, reducing NO_x emissions by an average of 24%. Biased firing (top row burners fuel-lean; bottom and middle row burners fuel-rich) reduced NO_x emissions by an average of 16%. Reducing the secondary air register setting from F-2 (maximum opening) to F-1 (partially closed down) on the reheat furnace increased NO_x emission levels by about 4% under normal firing operation (S_1) and reduced NO_x emissions by an average of 8% under biased firing operation (S_2). At full load, the lowest NO_x emission levels were obtained under test run No. 8 operating conditions of biased firing, low excess air, and closed down secondary air registers. This test condition produced 876 ppm NO_x, a reduction of 36% from 791 ng/J (1381 ppm) produced under baseline operation.

Twelve test runs were conducted at approximately 220 MWe, the maximum load achievable under staged firing (1 mill on air only) operation. Under normal firing operation (S_1), NO_x emissions were reduced by an average of 12% due to the load reduction from 290 to 220 MWe (24% reduction). Low excess air operation reduced NO_x emissions by an average of 9% under normal firing (N_1) and by 50% under staged firing (S_1). Staged firing (top row of burners on air only) was carried out with the secondary air registers of the top row of burners set at the maximum opening F=2, partially closed down F=1, or almost completely closed down position. As expected, the greatest reduction of NO_x emissions occurred when the top row secondary air registers were set at the maximum opening, F=2. Thus, the average reduction from the NO_x level for normal firing of 618 ng/J (1078 ppm NO_x) at 200 MWe were 24%, 43%, and 48% under staged firing (S_1) conditions when the secondary registers were set at closed, partially closed, and open positions, respectively. Test run No. 10 operating conditions of staged firing, low excess air and normal secondary air register settings (F-2) produced an average level of 240 ng/J (356 ppm) NO_x, or 57% below the 651 ng/J (1136 ppm) level experienced under baseline operation at about the same load.

Nine test runs were conducted at approximately 155 MWe which is the normal night-time low load conditions for this boiler. Under baseline operations at this load (top burners with air and coal off), NO_x emissions were 34% less than under full load operation. Low excess air and staged firing operation at this load again resulted in large NO_x emission reductions. Thus, low excess air combined with staged firing (run No. 26 conditions) lowered NO_x emissions by 61% from baseline operation at low load.

In summary, this wet bottom furnace boiler demonstrated significant NO_x emission reduction capabilities through combustion modification from the high baseline operating level of 793 ng/J (1383 ppm) at full load. Excess air level, firing pattern, and secondary air register setting were all important combustion control variables. The optimum operations at full load (290 MWe), intermediate load (220 MWe), and low load (155 MWe) produced NO_x emission levels and percent reductions of 502 ng/J (876 ppm) or 37%, 204 ng/J (356 ppm) or 74%, and 201 ng/J (351 ppm) or 75%, respectively.

2.2 Kewaren Station - Boiler No. 9
Public Service Electric and Gas Company (New Jersey)

A field test program was conducted to determine the NO_x emission reduction capabilities of the No. 9 330 MWe oil fired boiler at the Kewaren generating station, Kewaren, N.J. of the PSE&G Co. of New Jersey. Kewaren Boiler No. 9 is a Babcock and Wilcox, horizontally opposed fired unit with three rows of four burners in both front and rear walls. The high pressure feedwater heaters on this unit were out of service during the tests, limiting the maximum load to approximately 285 MWe (gross) output. A total of 24 runs were made on this unit. The major variables included in the experimental program were load (201-275 MWe net), excess air, flue gas recirculation (not into the windbox), various staged firing patterns, and the effect of a combustion improver additive supplied by Appollo Chemical Co. to the utility company for this boiler.

Figure 2 is a plot of NO_x emissions vs. oxygen in the flue gas for the 24 test runs. Referring to Figure 2 it may be noted that emissions on this unit are relatively low even at the higher excess air levels. At full load, uncontrolled NO_x emissions were estimated to be at the 220 ng/J (440 ppm) level. Because of stringent plume opacity limitations imposed by local authorities, operation at excess air levels below 2% O_2 was not possible. As shown by Figure 2, excess air level had a significant effect on NO_x emission levels for both normal and staged firing; 9 to 14 ng/J (16 to 24 ppm) NO_x reduction per 1% reduction in O_2 level. Staged firing reduced NO_x levels by 23% at 285 MWe. Staged firing patterns II, III and IV gave about equal results with 5 burners on air only giving slightly better results than 4 burners on air only. Lowering load by 26% reduced NO_x levels by 19%. Injecting flue gas into the lower level of the furnace had only a small effect (a reduction of 7%) on NO_x emissions. The combustion improver additive had no noticeable effect on NO_x emissions (data points No. 20 and 21).

2.3 T. H. Wharton Station, Gas Turbine No. 42
Houston Lighting and Power Company

T. H. Wharton's gas turbine No. 42 was tested in our current field test program to obtain data on NO_x emissions under baseline and wet control operations. This General Electric model MS 7001B gas turbine is of modern design, has a rated output of 50 MWe with a peak load of 54 MWe. It is equipped to fire gas or oil and has water injection capabilities with either fuel. Operating variables were gross load (0 to 55.5 MWe) and amount of water injected (0 to 2.1% of combustion air, or about 0 to 1.2 g H_2O/g fuel).

Flue gas samples were taken from the centers of 12 equal areas in the duct work leading to the stack. Gas samples were taken from each of the 12 sample points and analysed separately in the first test run on this unit (Run No. 10). As previously found in tests conducted by General Electric, there was an insignificant degree of gaseous stratification within the duct. For example, the O_2 level varied from 16.4% to 16.5%, and NO_x emissions varied from 44 to 46 ng/J (77 to 83 ppm) on an as-measured basis. Consequently, on the remaining test runs the gaseous samples from short, medium, and large tubes were composited into the 6 probes.

Figure 3 is a plot of NO_x emissions vs. gross load (MWe). Least squares regression lines have been drawn through the data points obtained with 0%, 0.75-0.80% and 1.5% water injection rates. The baseline NO_x emission level at full load (51 MWe) was 71 ng/J (127 ppm) compared to 76 ng/J (133 ppm) previously measured on Morgantown Station Unit No. 1 when fired at 54 MWe (1). Reducing load by 61% to 20 MWe resulted in reducing NO_x emission levels by 43% to 41 ng/J (76 ppm).

Water injection was extremely effective in reducing NO_x emission levels on this oil fired gas turbine. An 81% reduction was attained at full load when operating with 2.1% water injection. Lower water injection rates were less effective, but still reduced NO_x emission levels by substantial amounts as may be seen in Figure 3.

3.4 T. H. Wharton Station, Gas Turbine No. 43

T. H. Wharton's Gas Turbine No. 43, a General Electric model MS 7001B gas turbine is a duplicate of T. H. Wharton's GT No. 42 in every respect. Tests were conducted on this turbine while firing natural gas, the normal fuel used at this plant. Major operating variables included in the experimental program were gross load (20 to 56 MWe) and amount of water injected (0 to 1% of the combustion air, or about 0 to 0.5 g H_2O/g fuel). Since inlet air relative humidity had been shown to have a significant effect on NO_x emission levels, measurements of this variable were also included. Flue gas samples were taken from the centers of four equal areas from four probes.

Figure 4 is a plot of the NO_x emissions vs. gross load for the 10 test runs conducted on Unit No. 43. Linear, least squares regression lines have been drawn through the data for 0%, 0.5% and 0.75% water injection rates. As expected, both gross load and level of water injection has a significant effect on NO_x emission levels. From a baseline NO_x emission level of 42 ng/J (73 ppm, 15% O_2 basis) at 54 MWe, a load reduction of 51% (to 20 MWe) reduced the NO_x emission level by 45% to 23 ng/J (40 ppm). Thus, the percent reduction in NO_x level is less than proportional to the percent reduction in load.

Water injection had a larger influence on NO_x emissions than load reduction. Injecting water at rate of 1% of the air mass flow decreased NO_x emission levels from 74 ppm to 25 ppm, or by 66% at a gross load of 56 MWe. Combining both load and water injection into a single linear multiple regression analysis resulted in the following equation:

$$\text{PPM } NO_x \text{ (15\% } O_2 \text{ basis)} = 21 + 0.92 \text{ gross load (MWe)} - 52.2 \text{ (\% water injected)}$$

Ninety-seven percent of the variation in NO_x emission levels are related to these two operating variables.

Figure 5 is a plot of the 9 test runs conducted at about full load (52 to 57.5 MWe). The vertical axis is PPM NO_x (15% O_2, dry basis) and the horizontal axis is % water injected. A least-squares curve could be fitted based on the correlation of Shaw (5) to these data to produce the following relationship:

$$\text{PPM } NO_x \text{ (15\% } O_2\text{, dry basis)} = 70.3e^{-1.007 (\% H_2O)}$$

As shown by the smoothness of the curve in Figure 5, a very good fit was obtained with $r^2 = 0.996$.

3.5 Gulf Power Company, Crist Station, Boiler No. 7

The No. 7 boiler at the Crist Station of the Gulf Power Company in Pensacola, Florida is a horizontally opposed fired, pressurized unit built by the Foster Wheeler Energy Corporation. This boiler, as will be discussed later in this paper, was selected for long-term testing of the external corrosion of furnace tubes that may result from staged firing of high sulfur coal. The unit has a rated capacity of 500 MWe with superheat and reheat temperatures

of 811/811 K (1000°/1000°F), respectively. Six pulverizers supply pulverized coal to 12 burners each in the front and rear walls. Burners are arranged in 3 vertical rows in each wall with 4 burners in each row for a total of 24 burners. Operating variables included in the experimental field test design were: gross load (full load and medium load), excess air level (normal and high), staged firing patterns (including firing top burners lean and lower burners rich), with lower burner registers closed down to 40% open, and top row burner registers set at 80% open.

Figure 6 is a plot of NO_x emissions vs. flue gas O_2 for the tests conducted on this boiler. Linear, least squares lines were calculated and drawn through the data representing S_1 (normal firing at 460 to 520 MWe), S_2 (top burners lean at 430-450 MWe) and S_3 (top burners on air only at 410-440 MWe) operations. Baseline NO_x emissions under full load, normal excess air (1.6% flue gas O_2) were calculated to be 588 ng/J (1025 ppm). Biased firing, S_2 operation at 10% excess air reduced NO_x emissions to an average of 281 ng/J (490 ppm) at 10% excess air. As expected, low excess air and staging of the combustion process has a considerable effect on reducing NO_x emissions from this boiler, in agreement with results obtained on other pulverized coal fired units tested in this program.

2.6 East Kentucky Power Cooperative, Inc. John Sherman Cooper Station, Boiler No. 2

The Cooper Station, No. 2 boiler is a front-wall fired Babcock and Wilcox designed boiler rated at 200 MWe (gross load) and 703 t/h (703,700 Kg of steam per hour). Six Babcock and Wilcox Type EL pulverizers (using the ball bearing principle for grinding) feed 18 burners arranged in five rows. The furnace has a width of 12.8 m (42 ft.) and measures 7.1 m (24 ft.) from front wall to rear wall. Heating surface measurements are: boiler 385.8 m^2 (4,151 $ft.^2$), furnace 1981.1 m^2 (21,150 $ft.^2$), primary superheater 6370.2 (68,575 $ft.^2$), secondary superheater 664.8 m^2 (7,157 $ft.^2$), reheat superheater 2708.6 m^2 (29,158 ft.) and economizer 2717.9 m^2 (29,258 $ft.^2$), respectively. Superheat steam outlet temperature 811 K is (1005°F) at 12.9 MPa (1890 PSI) pressure. Reheat outlet steam temperature is 811 K (1005°F) at 3.1 MPa (445 PSI) pressure.

This unit was selected for field testing as a candidate for a second long term corrosion test on a front wall, high sulfur coal fired boiler representative of the design practices of B&W. The proximate analysis of the coal used in designing the boiler was 8% moisture, 33% volatile matter and 46.5% fixed carbon. Ultimate analysis components were 12.5% ash, 4.5% S, 4.2% H, 61.5% C and 1.2% N. Because of local regulations, this unit will be forced to fire low sulfur coal, a factor that tends to disqualify this unit as a candidate for long term corrosion testing.

A statistically designed experimental test program was conducted on this boiler to characterize emission levels using key operating variables of gross load (MWe), excess air, secondary air register settings, and staged firing patterns including firing top row burners lean, and bottom burners rich.

Figures 7 and 8 are plots of ppm NO_x vs. % oxygen for the data obtained in 32 gaseous emission test runs. Figure 7 presents data points collected at high loads of 166 to 227 MWe while Figure 8 presents data for lower boiler loads of 121 to 155 MWe. Least squares regression lines have been drawn through the data representing each firing pattern tested. There is somewhat more scatter of the data points around these lines than usually encountered. This is likely to be due to the following two reasons. First, some of the test runs were conducted when the boiler was operating under Automatic Dispatching System (ADS), i.e. fluctuating loads. Boiler loads were largely determined by East Kentucky Power Cooperative, Inc. system demand. Since Cooper No. 2 unit is the most flexible unit in the system, its electric output is controlled by ADS. Second, data have been combined for a wider range of loads than usual, accounting for the wider scatter.

Referring to Figure 7, it can be seen that, as expected, excess air has a highly significant effect on NO_x emission levels. At high loads (150-227 MWe), NO_x emissions were reduced by an average of 38 ng/J (66 ppm) and 36 ng/J (62 ppm) for each 1% drop in average flue gas oxygen content under S_{11}, normal firing operation and S_{22}, top burners fired lean operation, respectively. Similar results are shown in Figure 8 for the lower load test results. Baseline operation at high loads resulted in 330 ng/J (576 ppm NO_x) at 20% excess air, while low excess air, staged firing reduced NO_x emission levels to a low of 246 ng/J (429 ppm), a 26% reduction.

Under low load operation (150 to 155 MWe), as shown in Figure 8, NO_x emissions increased when the heat release per active burner was increased. For example, test run 45 (15 active burners and 150 MWe load) produced NO_x emissions of 362 ng/J (631 ppm), while at about the same load (155 MWe) test run 41 (18 active burners) produced only 330 ng/J (567 ppm) NO_x. There are several firing patterns for low load operation that are capable of reducing NO_x emission levels to below 229 ng/J (400 ppm). Operating with the top row burners on air only, however, is more effective in reducing NO_x emissions than operating with top row burners firing lean.

3.7 Colorado Public Service Company, Pueblo, Colorado
Comanche Station, No. 2 Boiler

Comanche No. 2 unit is a horizontally opposed fired, balanced draft Babcock and Wilcox designed boiler equipped with overfire air ports for controlling NO_x emission levels. Each of the four pulverizers feed eight conventional, circular register burners arranged in four rows of four burners each in the front and rear walls of the furnace. There is a single row of four overfire air ports above the top row of burners in both the front and rear walls of the furnace. Secondary air is fed to the burners through three compartmentalized wind boxes arranged so that dampers control the volume of air fed to the lower two rows of burners, upper two rows of burners, and overfire air ports of both front and rear walls. This boiler has a maximum continuous rating of 1150 t/h (1,150,436 kg/hr of steam at 350 MWe). Steam temperatures and pressures at the superheater and reheater outlets are 814 K (1005°F) at 17.3 MPa (2500 psig) and 814 K (1005°F) at 3.8 MPa (551 psig) respectively. The furnace volume is 7590 m^3 (268,000 ft^3). Total heating

surface is 31,264 m^2 (336,350 ft^2) of which 25,904 m^2 (287,860 ft^2) is convection surface.

Predicted boiler efficiency is 86.57%, based upon the following coal specifications. Proximate analysis - 29.0% moisture, 33.4% volatile matter, 32.4% fixed carbon and 5.2% ash; Ultimate analysis - 5.2% ash, 0.6% sulfur, 4.8% hydrogen, 47.3% carbon, 29.9% water, 0.9% nitrogen and 13% oxygen; HHV = 4586 cal/g (8250 BTU per pound); grindability index 55, and ASTM ash softening temperature of 1450 C (2150°F) at reducing conditions.

This boiler was selected for field testing because it represents an example of a NSPS unit manufactured with built-in second stage air ports, a NO_x control approach deemed suitable for low sulfur Western coal firing by its manufacturer. Operating variables included in the experimental design were: gross load (full load and minimum load while using all 6 mills), excess air level (normal and high) and overfire air dampers (0 to 100% open). Secondary air registers were maintained at normal opening (about 65%) and mill fineness was maintained at the normal level. Four probes, each containing three sampling tubes were placed in the ducts downstream of the economizer, and positioned to sample gases from the centers of 12 equal duct areas.

Figure 9 is a plot of NO_x emissions vs. the degree of opening of the overfire air dampers. Lines have been drawn through the data representing three different operating conditions: upper line = full load at high excess air, middle line = full load at normal excess air, and lower line = reduced load at normal excess air. Figure 10 is a plot of NO_x emissions vs. oxygen in the flue gas for data obtained in full load test runs.

Baseline operation (0% open overfire air ports and normal excess air) at full load produced NO_x emissions of 416 ng/J (726 ppm). This relatively low level for a 350 MWe unit can be partially accounted for by the low nitrogen (nominally 0.9%) and high moisture contents (29%) of the coal. Full use of the overfire air ports (100% open) reduced NO_x emissions by 62% to 159 ng/J (278 ppm) from baseline operation at full load. Partial use of overfire air ports gave intermediate levels of NO_x reductions: 50% reduction at 80% OFA, 47% reduction at 60% OFA, 47% reduction at 40% OFA, and 41% reduction at 20% OFA. Increasing excess air from normal (4.5% excess O_2) to high (5.2 to 5.7% excess O_2) increased NO_x emissions by 25 to 34% under full load operation. Thus, excess air, as expected, has a large influence on NO_x emission levels. Reducing boiler gross load from 350 MWe to 275 MWe (23%) reduced NO_x emissions by an average of 8%. This result is in line with results obtained on other pulverized coal fired boilers tested in this study.

SECTION 3

POTENTIALLY ADVERSE SIDE EFFECTS OF "LOW NO_x" OPERATIONS

An inevitable consequence of operating a coal fired boiler with staged firing and reduced excess air for NO_x emission control is the change from an oxidizing to a net reducing atmosphere in the region of the lower burner rows of the furnace. Under these conditions flames lengthen out, become dark and smokey, and there is a tendency toward incomplete combustion. Potentially, there may be a change in particulate emissions due to burnout problems; particle size distributions could change adversely, resulting in enhanced fine particulate emissions and affecting the efficiency of collector devices; boiler efficiency may decrease as a result of increased amounts of unburned combustibles; flame patterns could change causing problems due to instability or impingement; increased slagging of the furnace may be experienced as a result of lower ash softening temperatures under reducing conditions; and, perhaps foremost, particularly when firing high sulfur content coals, slagging and external corrosion of the furnace tubes may increase as a result of the reducing conditions of the furnace atmosphere. Studies on these potential side effects have been conducted by Exxon Research under EPA Contracts No. 68-02-0277 and 68-02-1415, the results of these studies [2,3] indicated that only external corrosion of the furnace tubes appeared to be a significant problem for the coal fired boilers tested. In the present paper, the extension of these studies to additional utility boiler field studies is summarized.

3.1 Particulate Emissions

Staging the combustion process and decreasing excess air levels to reduce NO_x emissions produces longer, "lazier" flames with a tendency toward incomplete combustion. Any increase in unburned carbon as a consequence of "low NO_x" operation would have a corresponding adverse effect on boiler efficiency and might tend to increase particulate emissions from the boiler. Particle size distribution might also be affected by this type operation which could have an adverse effect on precipitator performance. These problems have been the subject of past Exxon Research field studies [2] [3] which concluded that no significant changes in particulate mass loading or particle size distribution could be observed resulting from staged firing of coal in the utility boilers tested.

Table I presents particulate mass loading data obtained in recent studies which are in typical agreement with the results obtained in the prior programs. These data were obtained using EPA Method 5 sampling trains for particulates.

The data summarized in Table I was obtained on the pulverized coal fired, No. 1 boiler at the Mercer Station, and on the oil fired No. 5 boiler at the Sewaren Station of PSEG Co. of New Jersey. Comparing the low NO_x data with baseline results it can be seen that there are no significant differences in particulate mass loading for Mercer Boiler No. 1. Particulate mass loading results for oil firing of Sewaren Boiler No. 5 are, as expected, considerably lower than the levels measured in coal firing. This is due to the low ash content of the fuel oil fired. Interestingly, for the oil fired boiler particulate emissions measured under baseline and low NO_x firing conditions are essentially identical.

Particulate size distribution data are presented in Table II. The results for the coal fired Mercer Boiler No. 1 are typical of the particle size distribution information obtained on other coal fired units tested in this program. Note that there appears to be no significant difference in the size distribution of particulates produced under baseline and low NO_x operations, respectively. Consequently, the previous conclusion is further supported that "low NO_x" firing of coal does not affect particle size distribution adversely. This observation is especially noteworthy in regard to the submicron, respirable particulate size range.

The particle size distribution data obtained on the oil fired Sewaren Boiler No. 5 is interesting in two respects. First, it agrees directionally with the results for coal firing, i.e., low NO_x firing appears to result in only minor changes, if any, compared with baseline conditions. Second, the fraction of particulates in the submicron (especially in the $\leq$ 0.5 μm) size range is larger than for coal firing. This result may be indicative of the mechanism of particulate formation through cenospheres in oil firing.

3.2 Boiler Efficiency

The effect of combustion process modification on boiler performance was investigated and evaluated in prior Exxon Research field studies where particulate data were obtained under baseline and optimum "low NO_x" firing conditions. A small tendency for particulate carbon content (unburned combustibles) to increase with "low NO_x" firing was noted in these earlier studies [2], especially in front wall and horizontally opposed fired boilers. An increase in unburned carbon should result in lower boiler efficiency but this adverse side effect did not materialize in the previous studies due to the offsetting effect of low excess air operation under low NO_x operating conditions which increases boiler efficiency because of reduced stack losses. These results were confirmed in subsequent field studies [3].

Table III summarizes boiler efficiency results that are typical of those obtained in prior field test programs. Table III shows that the Mercer No. 1 boiler under low NO_x conditions operated at exit gas O_2 levels nominally below 2%, whereas under baseline operation O_2 levels were in excess of 3%. The particulate carbon content under low NO_x conditions was somewhat higher than under the baseline conditions. The calculated values of the boiler efficiency were, however, essentially the same for both baseline and "low NO_x" operations, i.e. about 90%. These results again confirm the offsetting influence of low excess air operation (with low NO_x firing) on boiler efficiency, to compensate for the loss in efficiency due to increased carbon losses.

3.3 Slagging

As mentioned previously, low NO_x combustion modifications for NO_x emission control result in a change in the furnace atmosphere adjacent to the lower burners from oxidizing to net reducing conditions due to staging of the combustion process and a reduction in overall excess air levels in the boiler. A potential consequence of "low NO_x" operation could be an increased tendency toward slagging of the furnace walls in the vicinity of the lower burners and in the critical hopper slope areas. Ash fusion temperatures in most coals decrease by approximately 111 K (200°F) when measured under reducing conditions. Thus, if a reducing atmosphere prevails in the bottom of the furnace under low NO_x conditions, the tendency would be for the ash to melt quicker and be more fluid and sticky, fouling the furnace surfaces more readily.

Most coal fired boilers are designed for operation at 15 to 25 percent excess air with oxidizing atmospheres prevailing in the furnace. In most boilers, furnace surfaces approximately 3.0 m (10 ft.) above the burners are adequately covered with slag blowers to remove any ash accumulating on, and blanketing the furnace heat transfer surfaces. Under normal design conditions operation of these blowers two or three times per day will keep the furnace tubes clean. If lower ash fusion temperature coal is burned, as happens on occasion, these areas will slag more rapidly requiring more frequent operation of the slag blowers. Operating a boiler under "low NO_x" conditions could have a similar effect. However, low NO_x operation results in changes in the furnace atmosphere in the lower regions of the furnace where slag blowers normally are not installed. Potentially, therefore, an adverse side effect of "low NO_x" firing could be an increased tendency towards slagging of the furnace surfaces where no means exist for removal of such ash accumulations. As a consequence, boiler availability could be impaired by forced shutdowns to remove the accumulated slag. In instances where this occurs, a solution to this problem would be the installation of additional slag blowers in the lower areas of the furnace to remove accumulations before they have a chance to build to critical proportions.

In past Exxon Research field test programs [2] [3] utility boilers have been operated for periods up to 1000 hours under low NO_x firing conditions without noticeably increasing slagging conditions or causing boiler shutdowns. More frequent use of existing slag blowers may have been necessitated on occasions, but, if so, increased slagging problems were not apparent. The lower furnace surfaces, where no removal facilities exist, also presented no unusual increased slagging problems during these tests. Accordingly, under most conditions studied, it appears that "low NO_x" operation did not increase slagging conditions to a point where normal removal facilities could not handle the deposits.

3.4 Flame Problems

Pulverized coal combustion systems inherently are much more complicated than those used for oil or gas firing. Liquid or gaseous fuels can be handled, distributed and controlled uniformly to each burner with relative ease. On the other hand, pulverized coal systems require pulverizers, first, to grind the coal to the required fineness and then distribute the fuel to the burners

pneumatically. On utility boilers each pulverizer normally serves 4 to 6 burners through huge pipes. The fuel flow to these burners is virtually always non-uniform. In addition, because of problems of erosion, there are no regulating valves in the burner lines which might be used to balance fuel flow between burners, as is possible with oil or gas fuels. Furthermore, constant change is gradually, but continually taking place in the combustion parameters due, in most part, to pulverizer wear. Combustion control in a pulverized coal system, because of these factors, is considerably more difficult than with other types of firing systems.

In the early days of the pulverized coal combustion system development, flames were unstable and sensitive to changes in firing rate. Flameouts occurred frequently and difficulties were experienced with flame impingement on the side and rear walls of the furnace. Unburned combustibles (carbon loss) problems, associated with mill grinding capabilities, were also of serious concern. Therefore, there was legitimate concern on the part of the utility industry that low excess air and/or staged firing of pulverized coal in utility boilers could result in flame control problems. However, the accumulated experience of the Exxon Research field studies of combustion modifications for NO_x emission control on over 30 pulverized coal fired utility boilers shows that relatively few flame problems had been encountered. Flame instability or impingement problems have not manifested themselves in these studies, and increases in unburned combustibles, as discussed previously, have been found to be minor, resulting in negligible effects on boiler efficiency.

3.5 Corrosion Probe Measurements

Nitrogen oxide emissions are limited most effectively in utility boilers by staging the combustion process and maintaining the overall excess air level at minimum values consistent with safe, efficient operation. Staging the firing pattern consists of first, burning the fuel in the lower regions of the furnace under fuel-rich or (substoichiometric air supply) conditions, followed by second stage air addition above the primary combustion zone to complete burnout of the remaining combustibles. Furnace tube wall corrosion potentially could occur or be aggravated by operating a utility boiler at "low NO_x" firing conditions. Even though overall excess air is maintained at a reasonable level under "low NO_x" operation, conditions in the first stage combustion zone may approach levels as low as 80% of stoichiometric. Atmospheres at the furnace sidewalls where corrosion could take place under these conditions, might well be even more reducing. For normal firing the atmosphere in the furnace is oxidizing. However, under "low NO_x" staged firing conditions using upper burner rows as overfire air ports, only the top area of the furnace is under oxidizing conditions while the lower region (at the middle and bottom burners) is now in a reducing atmosphere, and it is this condition which may lead to potentially aggravated furnace tube external corrosion problems.

To gain insight into this potential problem area, corrosion probes have been used by Exxon Research in two EPA sponsored programs, Contracts No. 68-02-0227 (2) and 68-02-1415 (3), respectively. As discussed elsewhere (2) (3), the design of the corrosion probes was based on information supplied by Combustion

Engineering, with appropriate modifications for this work. Essentially, the design consists of a "pipe within a pipe", where the cooling air from the plant air supply is admitted to the ring-shaped coupons exposed to furnace atmospheres at one end of the probe, through a 19 mm (3/4 inch) stainless steel tube roughly centered inside of the coupons. The amount of cooling air is automatically controlled to maintain the desired set-point temperature of the coupons. The cooling air supply tube is axially adjustable with respect to the corrosion coupons, so that the temperatures of coupons can be balanced. Because the cooling air returns along the 63.5 mm (2-1/2 inch) extension pipe and discharges outside of the furnace, the cooling air and the furnace atmosphere do not mix at the coupon location.

The approach used for measuring corrosion rates in the initial program was to expose corrosion coupons installed on the end of probes inserted into available openings located near "vulnerable" areas of the furnace under both baseline and low NO_x firing conditions. Coupons were fabricated of SA 192 carbon steel, the same material as that used for furnace wall tubes. Exposure of the coupons for 300 hours at elevated temperatures of 742 K (875°F) (higher than normal furnace tube wall temperature of about 489 K (600°F) was chosen in order to deliberately accelerate corrosion so that measurable values could be obtained. Coupons were also mildly acid pickled to remove the existing oxide coating prior to exposure to eliminate differences potentially caused by surface conditions. The conclusion of these earlier corrosion probing tests was that no major differences in corrosion rates could be found between coupons exposed to low NO_x firing conditions, compared to coupons exposed under normal boiler operating conditions. Coupon corrosion rates were, however, considerably higher under baseline and low NO_x conditions than those corresponding to normal furnace tube wastage rates, because of the accelerated nature of these corrosion probing tests.

Significant changes were made in the conditions for measuring corrosion rates in subsequent field tests to better relate measurements obtained with corrosion probes to actual furnace waterwall corrosion. The approach was similar to the earlier work, but with several important differences. First, corrosion coupons, which were all fabricated and machined in the same manner, were no longer mildly acid pickled but instead, were dipped in acetone, and air dried prior to weighing to removal any oil deposited during machining. Second, coupon temperatures were controlled at temperatures approximating those of the furnace waterwall tubes, 601-650 K (625-725°F) to more closely approximate actual furnace conditions. Third, three coupons were installed on each probe, to increase the amount of data obtained compared with only two coupons per probe in the prior program. Time of exposure (300 hours) was held the same so that the results of the corrosion probing runs could be compared to the earlier work. Other test conditions were also kept the same, i.e., probes were inserted through openings in the furnace wall as close as possible to vulnerable furnace areas, the analytical procedures used were also the same in both programs, etc. Thus, each coupon was visually inspected after exposure and was photographed to record its appearance. Scale was then removed from the outside diameter surfaces by dry honing of the inside diameter surface scale after which the coupon was reweighed to determine the weight loss from the inside surfaces. Corrosion rates were then calculated as the loss in mils per year (m/yr) using the weight loss data, the combined exposure coupon areas, the metal and scale and densities, and the exposure time.

Using this approach, the coupon corrosion rates are considerably lower than those measured under accelerated conditions in the initial program. The lower and more consistent coupon corrosion rates measured in the latter program reflect the changes made in test procedures to more closely approximate actual furnace wall tube conditions. However, the rates are still an order of magnitude greater than the 1 to 3 mils per year corrosion rates that are expected for the wastage of actual furnace tubes under normal firing conditions. Therefore, the corrosion probing results are viewed as only a relative measure of corrosion tendency under baseline and low NO_x firing conditions. It was concluded from these studies that only long term corrosion measurements of actual furnace tube wastage could answer the question of the magnitude of corrosion rate increase caused by staged firing of utility boilers with pulverized coal. However, corrosion probe data and techniques may still be useful in the future if reliable correlations with actual tube wastage can be established.

SECTION 4

LONG TERM CORROSION TESTS

During the course of the corrosion probe investigations conducted by Exxon Research under EPA sponsorship, it became apparent that data obtained with probes could not provide an unequivocal resolution to the question whether external furnace tube corrosion might increase with "low NO_x" operation on utility boilers fired with pulverized coal. Even though "low NO_x" combustion conditions did not produce any major increases in corrosion rates as measured by corrosion probes, it was not only difficult to relate these data to actual tube wastage rates, but one could not rely on such information for boiler design and operation. From the power generation industry standpoint it is imperative that this question be resolved and, if corrosion is indeed a problem, engineering solutions are required for the application of "low NO_x" operation to coal fired boilers. A comprehensive corrosion investigation program, therefore, was undertaken in an attempt to settle this issue conclusively. Long term tests sponsored by the EPA have been undertaken in a joint cooperative venture by Exxon Research and Engineering Company, Foster Wheeler Energy Corporation, and the Gulf Power Company. These tests have been underway since June of 1976 on the No. 7 boiler at the Crist Station of Gulf Power Company in Pensacola, Florida. Three types of corrosion rate determinations are being employed:

1. Measurements on specially installed furnace tube panel test specimens.

2. Ultrasonic mapping of the thickness of the furnace tubes and test panels.

3. Corrosion probes exposed for varying times.

Details of these methods are discussed elsewhere [3]. The highlights of the long term corrosion test program are summarized below.

4.1 Test Panel Design, Installation and Measurements

Boiler manufacturers' experience indicates that external corrosion of furnace tubes occurs in areas in a largely unpredictable and random pattern, although the general problem areas are at the burner elevations of the furnace sidewalls. This presents a major problem in determining where to place the furnace corrosion panels to ensure that they are in areas where corrosion occurs. There is no ideal solution to this problem, and from an economic standpoint the number of panels used must, of necessity, be limited.

Eight corrosion test panels were installed in the No. 7 boiler at the Crist power station during May, 1976 at strategic locations believed to be most helpful in defining potential corrosion effects. Windows were cut out of the furnace walls the size of the corrosion panels and the sections removed were retained for future laboratory inspection. Panel and corrosion probe locations are shown in Figure 11. It can be seen that seven of the panels were installed in the left furnace side wall and one in the right wall. The reason for installing most of the panels in the one wall is to provide maximum areas of exposure to corrosion. Since the corrosion probe areas of the sidewalls are normally at the midpoint at the burner elevations, four of the panels (No. 1, 4, 5 and 6) were installed in this area. Three of these panels (No. 1, 4, and 5) are at the middle burner row elevation, and panel No. 6 is at the top burner elevation. Note that panel Nos. 4 and 6 are located in the middle of the sidewall where the most severe corrosion can be anticipated. Panel Nos. 1 and 2 are located in the hopper area where corrosion in other boilers occasionally has been experienced. Panels 7 and 8 in the left hand and right hand sidewalls, respectively, installed in the upper reaches of the furnace (above the burners), are expected to experience lower corrosion rates (oxidizing atmosphere) and will serve as "control" panels for comparison purposes. This scheme of panel arrangement was conceived to provide the maximum amount of data within the constraints of reasonable level of effort.

Each test panel is five (5) tubes wide by 1.5 meters (5 ft.) in length. Tubes 1, 3 and 5 were made of the same low carbon steel material as the furnace tubes; SA-210 grade A-1. Tubes 2 and 4 are SA-213 grade T-2, a higher grade alloy carbon steel expected to have greater resistance to corrosion than normal furnace tube material. The use of two materials will provide additional useful information on rates of corrosion which would not be available if only one material were used.

Prior to installation, the panels were characterized in the laboratory after fabrication. Thickness measurements were made ultrasonically at 1 inch intervals on the side of the panel exposed to the furnace and at 6 inch intervals on the opposite side, for control purposes. In addition, points near the end of the tubes were measured independently by an accurate micrometer on both sides of the panel, so that an independent measure of precision could be developed from paired mechanical vs. electronic measurements.

Examination of the test panels while still in place in the furnace is almost identical to that for wall tubes. Samples of corrosion products will be removed periodically from the tube surfaces by chipping, and the extent of metal loss is being determined by ultrasonic measurement. The major advantage of test panels is that they can be removed from the furnace and sectioned to give precise indications of metal loss and of the composition of corrodents.

Metallographic examination of the panel tube metal can provide important information. Such methods, by examining the grain structure after exposure, give a good indication of the mode by which corrosion is occurring and can detect incipient metal attack along grain boundaries not detectable otherwise. Sulfidation, in particular, can be shown by metallographic examination. Also, if the metal should have been overheated at any stage, the extent of spheroidization will provide a rough measure of this change in metal structure.

Two steps have been taken to obtain information characterizing corrosion panel exposure conditions. These include (1) measurement of corrosion panel tube metal temperatures and (2) analysis of the gaseous atmospheres in the location of the panels. Three thermocouples were installed in each panel (in the 1st, 3rd, and 5th tubes). The thermocouples are designed to measure the temperature of the tube as closely as possible to the surface exposed to the flame in the furnace. The objective is to determine whether any unusual temperature conditions may exist which would contribute to corrosion. Thirty gas taps were installed throughout the furnace area and in the front, rear and side walls including taps in the corrosion panels. Periodic surveys and analyses of the gases taken from these taps at different loads and combustion conditions will provide information to characterize the atmosphere in the furnace, especially under "low NO_x" operation.

4.2 Ultrasonic Tube Thickness Measurements

In order to determine the extent of potential furnace tube corrosion the tubes must be measured before and after prescribed periods of time. In the recent past highly accurate ultrasonic thickness measuring equipment was not available. Accuracy within 5 mils only was possible (3). Today, instruments are available capable of accuracy to tenths of a mil. In the program being conducted on the No. 7 boiler at the Crist Station, two Krautkramer-Branson CL 204 ultrasonic instrument gages, the most accurate currently available, are being used in making the measurements. Accuracy of these instruments is 0.01% of an inch, thus assuring that measurements to the nearest tenth of a mil are possible. This degree of accuracy is an essential feature for determining corrosion rates in a reliable fashion. Procedures and methods have been upgraded to achieve the highest degree of accuracy possible as experience with the instrument has been gained.

The condition of the tubes is a complicating factor requiring sand blasting, or some other suitable form of slag, deposit, or scale removal before reliable measurements can be made. Then the question remains after the tubes have been cleaned bare, are they now more susceptible to corrosion, and therefore no longer representative since oxide scales, coatings or protection have been removed? It is also difficult to relocate a spot previously measured for rechecking, and measurements at other places on the tube may be unreliable for comparison due to variations in tube manufacturing tolerances. Unfortunately, sandblasting, wire brushing or other means of cleaning to remove ash or slag coatings from the tubes down to the base metal, necessary for accurate thickness measurement, undoubtedly will remove any protective coating making the tube more vulnerable to corrosion at this spot.

To statistically eliminate bias in the results due to the greater corrosion vulnerability of tube areas previously cleaned and measured, a large number of measurements are taken at a given elevation at the beginning of the test in a random pattern, on some tubes exactly at the elevation, and on others slightly above and below the exact elevation. At the conclusion of the test, many measurements are repeated and center measurements are made exactly at the elevation on those tubes previously measured above and below the elevation.

Ultrasonic tube thickness measurements were made at six different furnace elevations in the No. 7 boiler at the Crist station in May 1976, after the corrosion test panels were installed. A second set of measurements were taken at the same elevations in October of 1976, after the boiler had been operating for 5 months under baseline operating conditions. These data will provide corrosion rate information for future comparison with similar data presently being obtained under "low NO_x" firing conditions. Figure 11, showing corrosion panel locations, also shows the six furnace elevations where ultrasonic tube thickness measurements were made. The only elevation on Figure 11 at which measurements were not made is elevation 30.4 m (99'-8"), the junction of the furnace with the hopper. Elevations 28.4 m (93'), 34.4 m (113'-8"), 36.9 m (121'-2"), and 39.5 m (129'-8") include all elevations in the furnace area where corrosion may be anticipated. Measurements at elevations 42.1 m (138'-2") and 48.1 m (157'-8") are in the oxidizing zone where corrosion is least likely to occur. These measurements will provide "control" information.

4.3 Corrosion Probe Measurements

Corrosion probes (as described in Section 3) are again being employed on the No. 7 boiler at Crist Station to obtain corrosion rate information concurrently with corrosion rate data taken by corrosion panels and ultrasonic tube measurements. The objective of these measurements is to establish correlation of actual tube wastage experience with corrosion probe data, so that confidence in the reliability of the less expensive corrosion probe methods may be achieved. Several changes, however, have been incorporated in the corrosion probe procedures to improve the program and to provide a greater amount of useful information. First, probes are being exposed for 30, 300, and 1000 hours, both under baseline and "low NO_x" firing conditions. The 30 hour exposure will provide data on initial corrosion and the 300 and 1000 hour information will show the effect of corrosion with time. Also, correlation with previous investigations on other boilers at 300 hour exposure should be possible. Second, special openings were incorporated in the furnace corrosion panels to accommodate the corrosion probes so that, for the first time, corrosion probes could be located in areas of greatest anticipated corrosion and in "control" areas.

4.4 Status of the Long Term Corrosion Tests

As indicated above, eight corrosion panels were installed in the No. 7 pulverized coal fired boiler at the Gulf Power Company's Crist power generating station in Pensacola, Florida, during May 1976. New openings were also provided in the furnace sidewalls during this outage for the more advantageous location of corrosion probes in areas vulnerable to corrosion, to better define the corrosion problem using this method of approach. At the beginning of the long

term corrosion test (May 1976), over 1000 ultrasonic tube thickness measurements were made on the No. 7 unit (including measurements of corrosion panel tubes) at the six elevations mentioned earlier. The unit was then run over the summer during the peak load demand period under baseline operating conditions for five months, until October 1976, when the boiler was taken out of service for a scheduled maintenance outage. Ultrasonic tube measurements were again made during the latter outage in accordance with the statistical plan developed for these tests. These results obtained will be subjected to detailed statistical analysis and compared to those that will be forthcoming from the low NO_x operation.

The No. 7 pilot boiler is now being operated under low NO_x conditions, and will continue this type of operation until the next scheduled maintenance outage in September/October 1977. At that time, the corrosion panels will be removed from the boiler (after about 1 year of low NO_x operation) and returned to the laboratory for re-measurement of the tubes and metallographic examination of the specimens. Ultrasonic tube thickness measurements will also be made at the previously prescribed elevations. These data, when compared to the measurements made in October 1976, should provide definitive information on seasonal furnace tube corrosion experienced under "low NO_x" operation. A comparison can then be made to actual wastage experienced under baseline conditions which should prove whether or not "low NO_x" firing leads to increased corrosion of the furnace tubes in this pulverized coal fired boiler.

Corrosion rate data have been taken under the baseline operating period and are currently being obtained under "low NO_x" firing conditions at exposures of 90, 800 and 1000 hours for correlation with actual tube wastage rates determined on corrosion panels and by actual furnace tube measurements.

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TABLE 1. PARTICULATE EMISSION TEST RESULTS
POWERED COAL AND OIL FIRED BOILERS

Location	Test No.	Firing Condition	Load, MW	Emissions				Dust Collection Efficiency % Mass (1.1 lb/ 10⁶ BTU)	at * Carbon on Particulate	Coal Ash Wt. %	EMF, Gen.	
				gr/ft³	lb/10⁶ BTU	kg/h	TP-TOP KPY					
	2		265	.31	0.55	1119	3.09	96.79	2.2	9.57	7567	22,420
	4		268	.39	0.64	1290	3.28	96.68	2.3	9.23	7615	22,788
	6		264	.37	0.57	972	2.74	96.44	2.1	11.00	7323	21,241
	1		261	.33	0.47	1036	2.64	96.14	3.0	9.57	7567	22,420
	3		268	.37	0.58	1240	4.17	95.69	2.7	9.23	7615	22,788
	5		264	.34	0.53	978	2.42	95.84	3.0	11.00	7323	21,241
	42		265	.004	.019	11.8	.03	—	—	—	—	—
	41		260	.004	.017	11.0	.03	—	—	—	—	—

* Sampling at air heater outlet upstream of collector devices

— Coal Firing

— Oil Firing

TABLE II. PARTICLE SIZE DISTRIBUTION, %[a]
(PUBLIC SERVICE ELECTRIC AND GAS COMPANY TESTS)

Size Range	Newport Station - Boiler No. 1[b]						Seaholm Station - Boiler No. 5[c]	
	Baseline			Low NO$_x$			Baseline	Low NO$_x$
	2	4	6	1	3	5	40	51
>2.5μm	84.8	86.1	81.9	88.6	90.7	80.8	84.6	80.9
2.5μm	2.7	4.4	2.8	3.2	2.9	4.7	4.9	7.0
1.5μm	2.4	2.4	3.5	2.1	0.5	2.7	3.7	2.0
1.0μm	1.9	1.0	0.9	1.3	1.1	2.4	1.1	1.5
0.5μm	1.9	1.5	3.1	1.1	1.0	0.4	1.3	1.7
<0.5μm	2.5	0.9	11.7	1.5	1.7	4.0	4.2	11.9

[a] Coal firing (Entrance No. 12)

[b] Oil firing (Entrance No. 5)

TABLE III. TYPICAL BOILER EFFICIENCY RESULTS

Company, Station	Boiler No.	Firing Mode	Test No.	Load, MW	% Ex.	NO_x Emissions at 3% O_2			Coal Ash, % (wt Basis)	% Carbon on Particulate	Boiler Efficiency, %

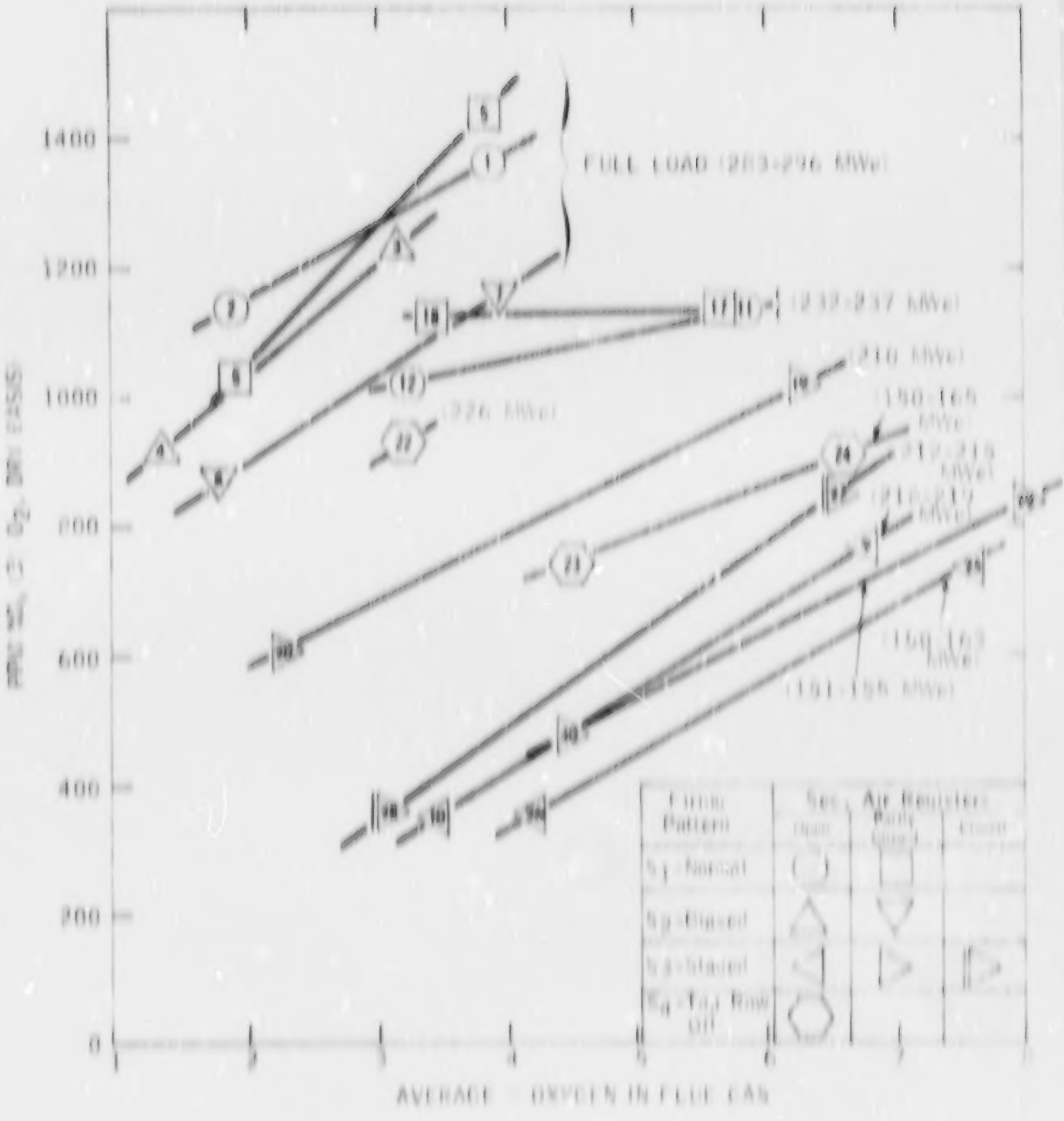


Figure 1: NO_x emissions measured for Reheat No. 1 boiler.

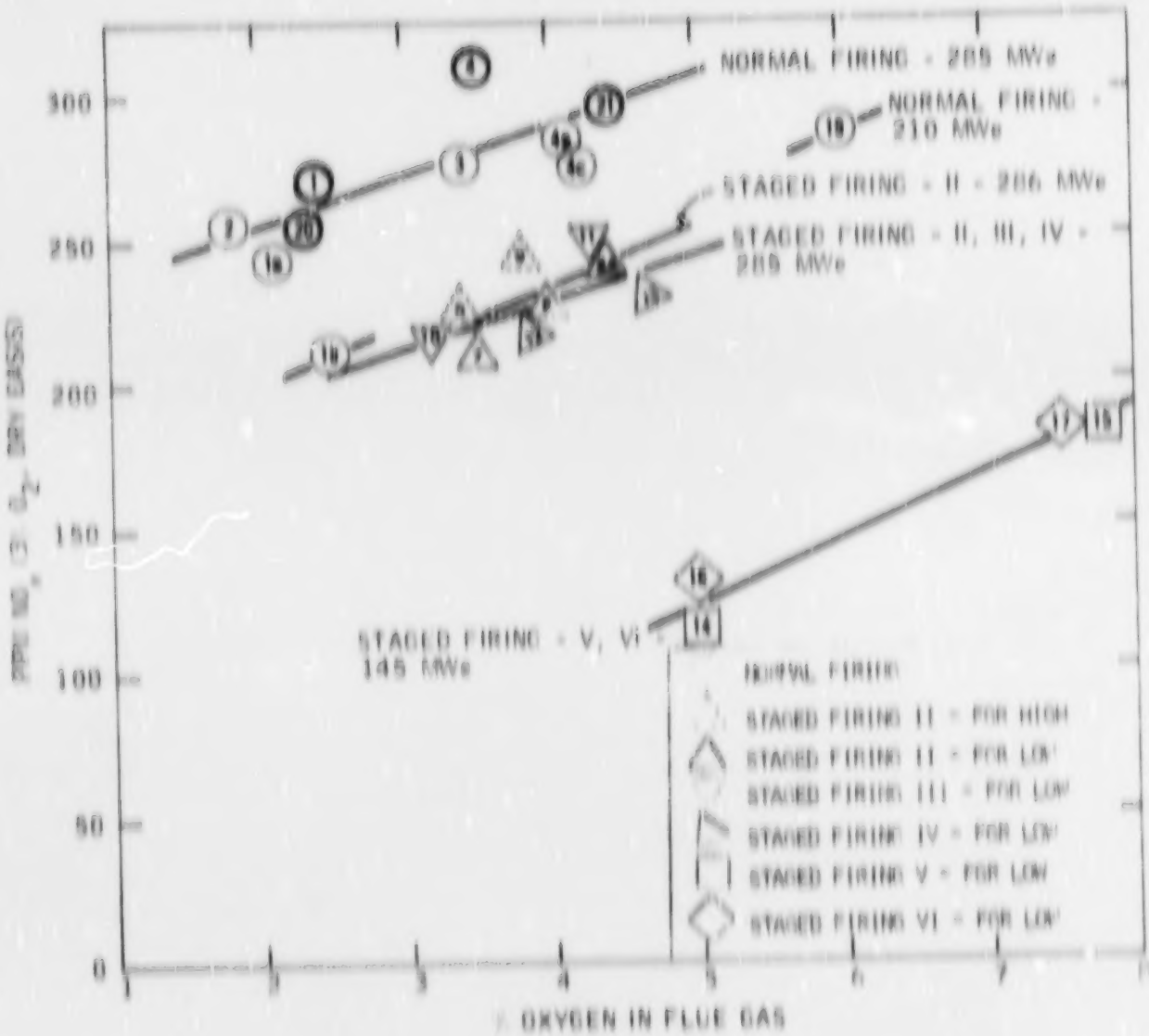


Figure 2: Effect of operating variables on NO_x emissions for oil fired boiler (Sawaren boiler no. 5).

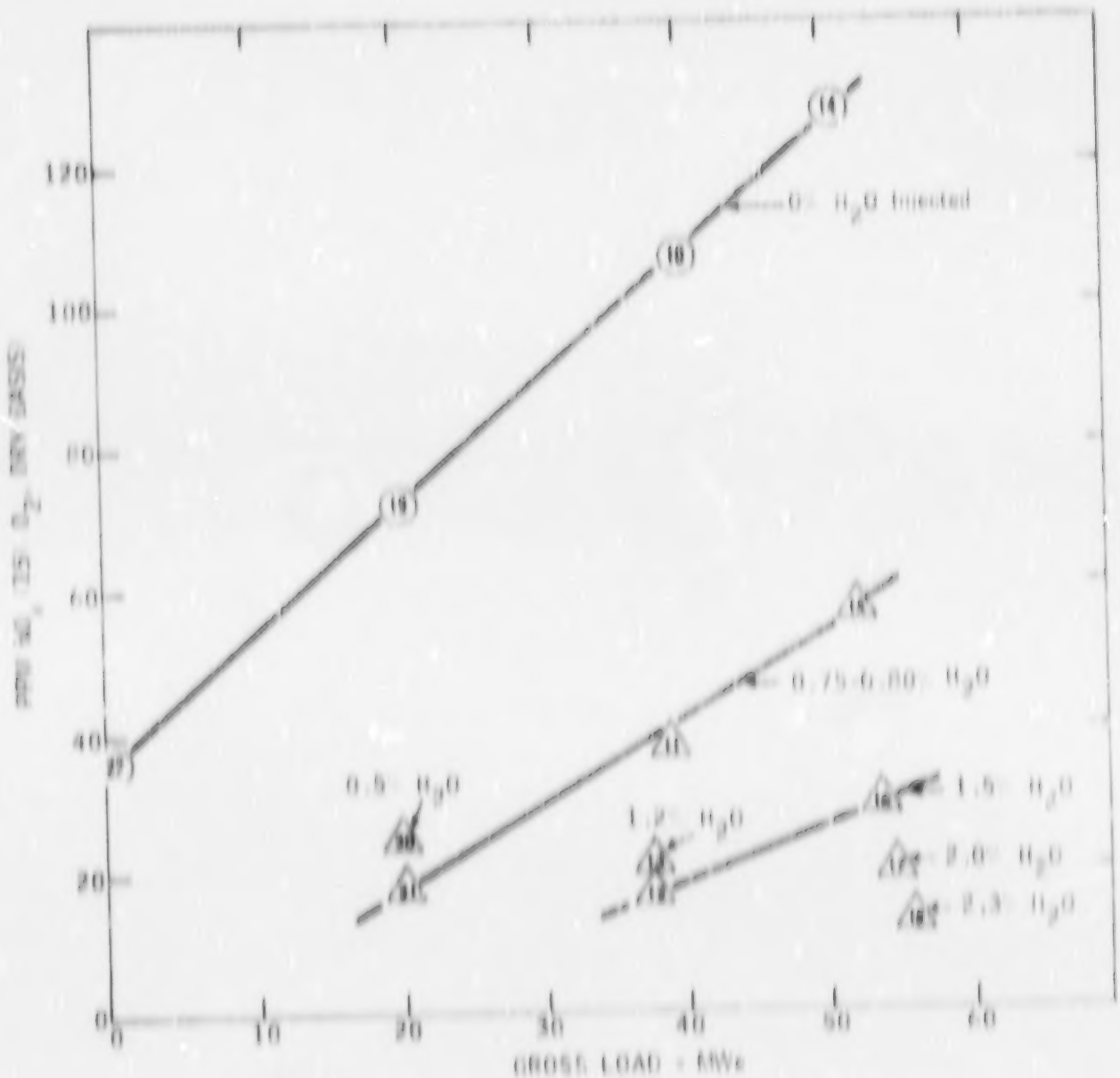


Figure 7. Effect of water injection on NO_x emissions from oil fired gas turbine (T. E. Wharton gas turbine No. 523).

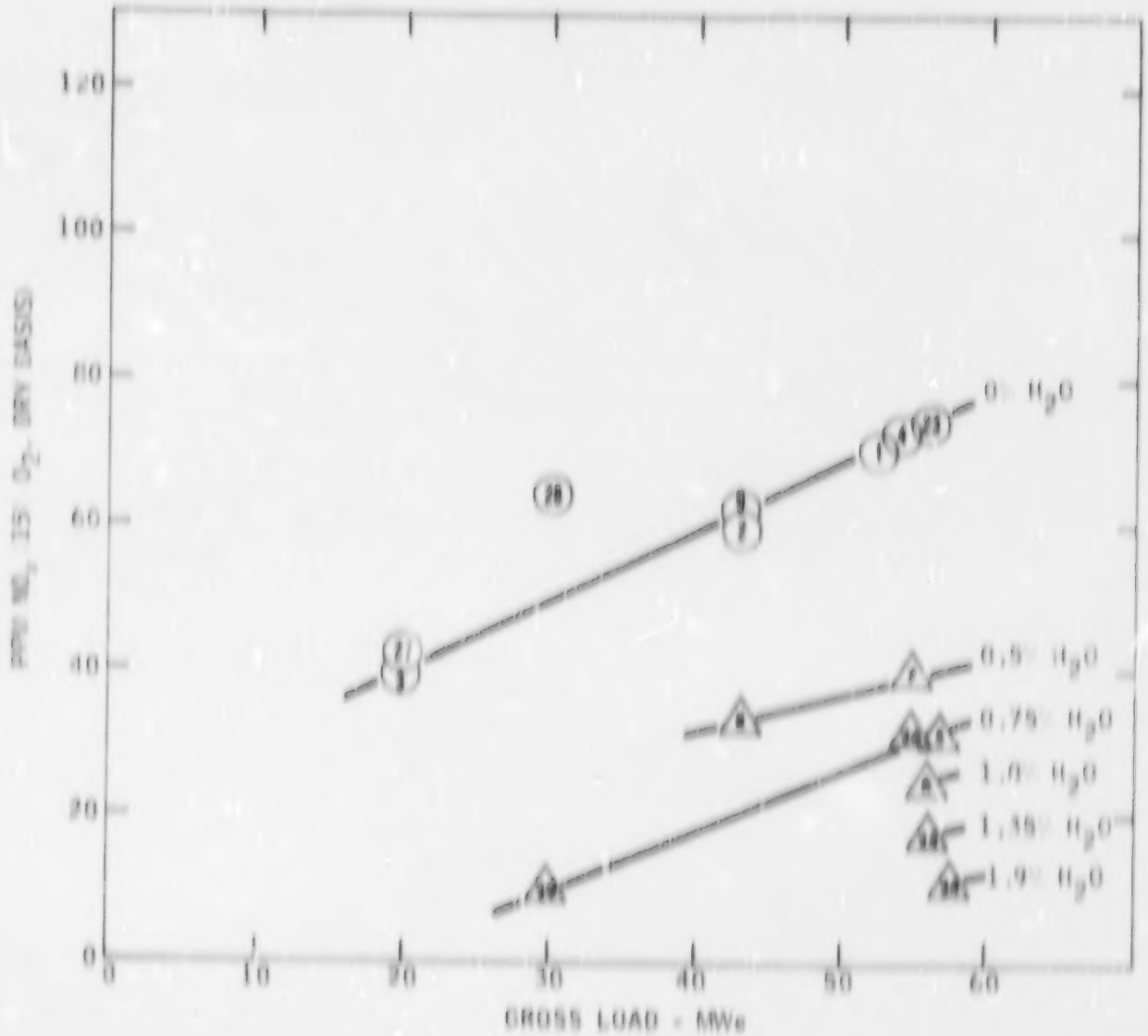


Figure 5. Effect of water injection on NO_x emissions from gas fired turbine (T. H. Wharton unit No. 51, gas fired).

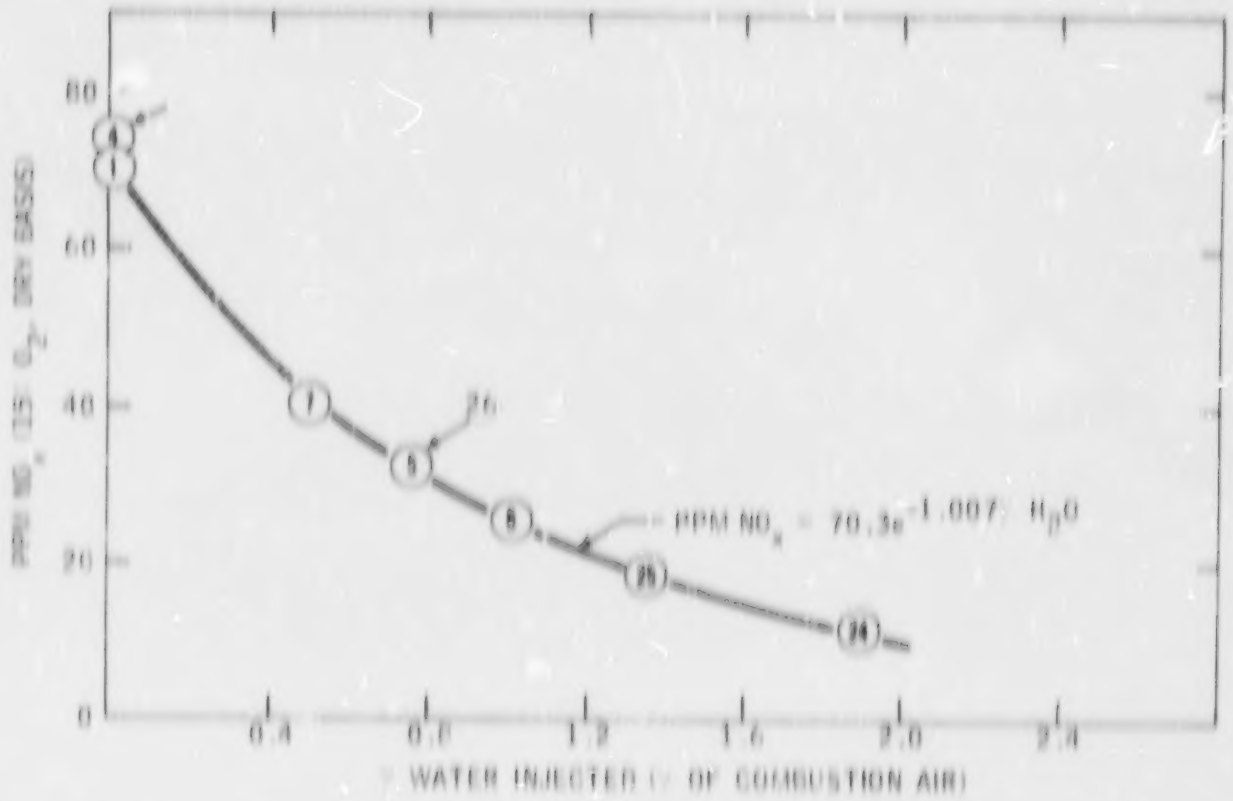


Figure 5. Correlation of NO_x emissions with water injection rate for natural gas fired gas turbine (Rhein-on ESP Wharton No. 53 unit).

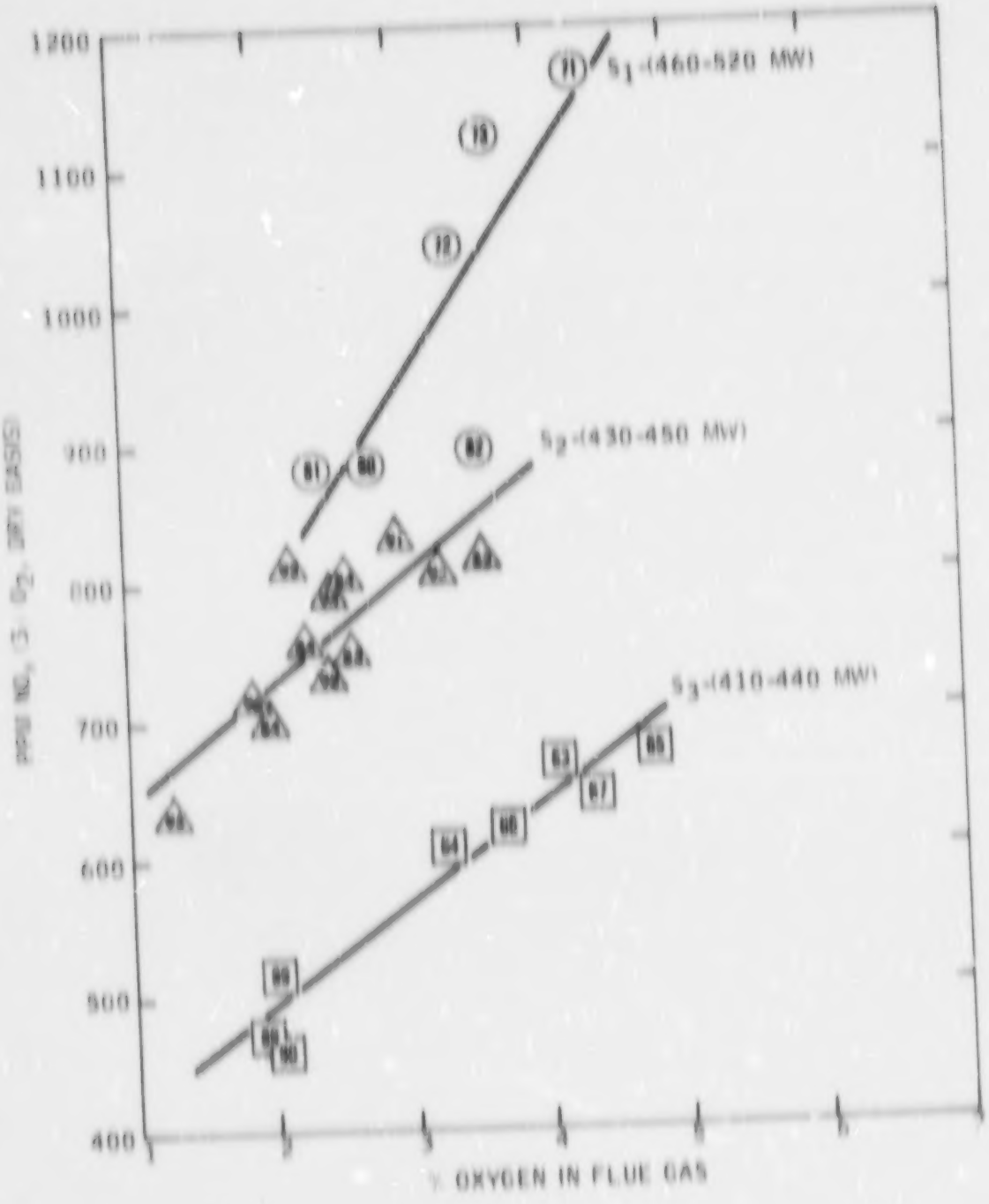


Figure 6: NO_x emissions measured for Test No. 7 boiler (A duct).

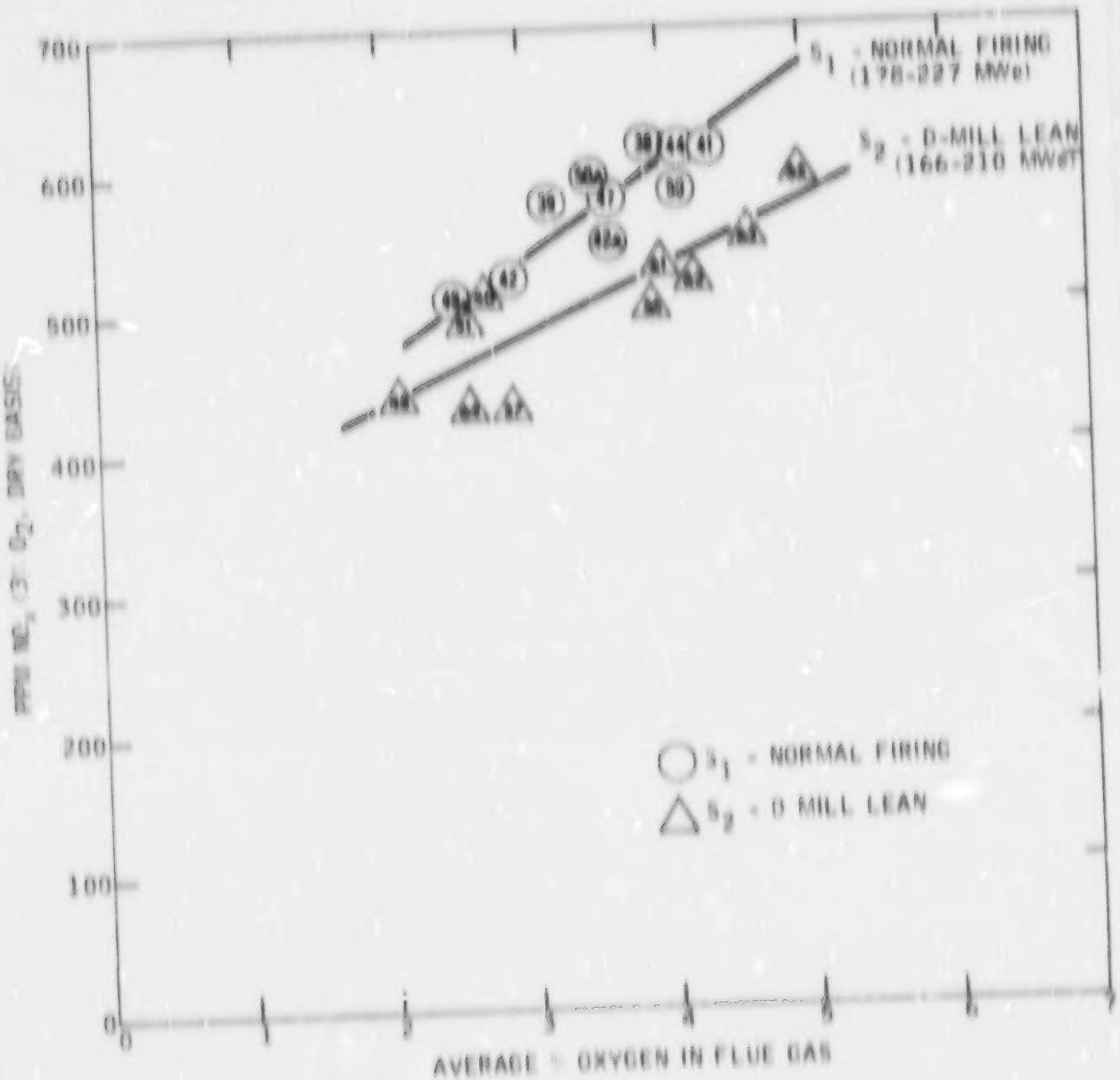


Figure 7: Effect of excess air and staging on NO_x emissions (Cooper No. 2 boiler - 166 to 227 MWe).

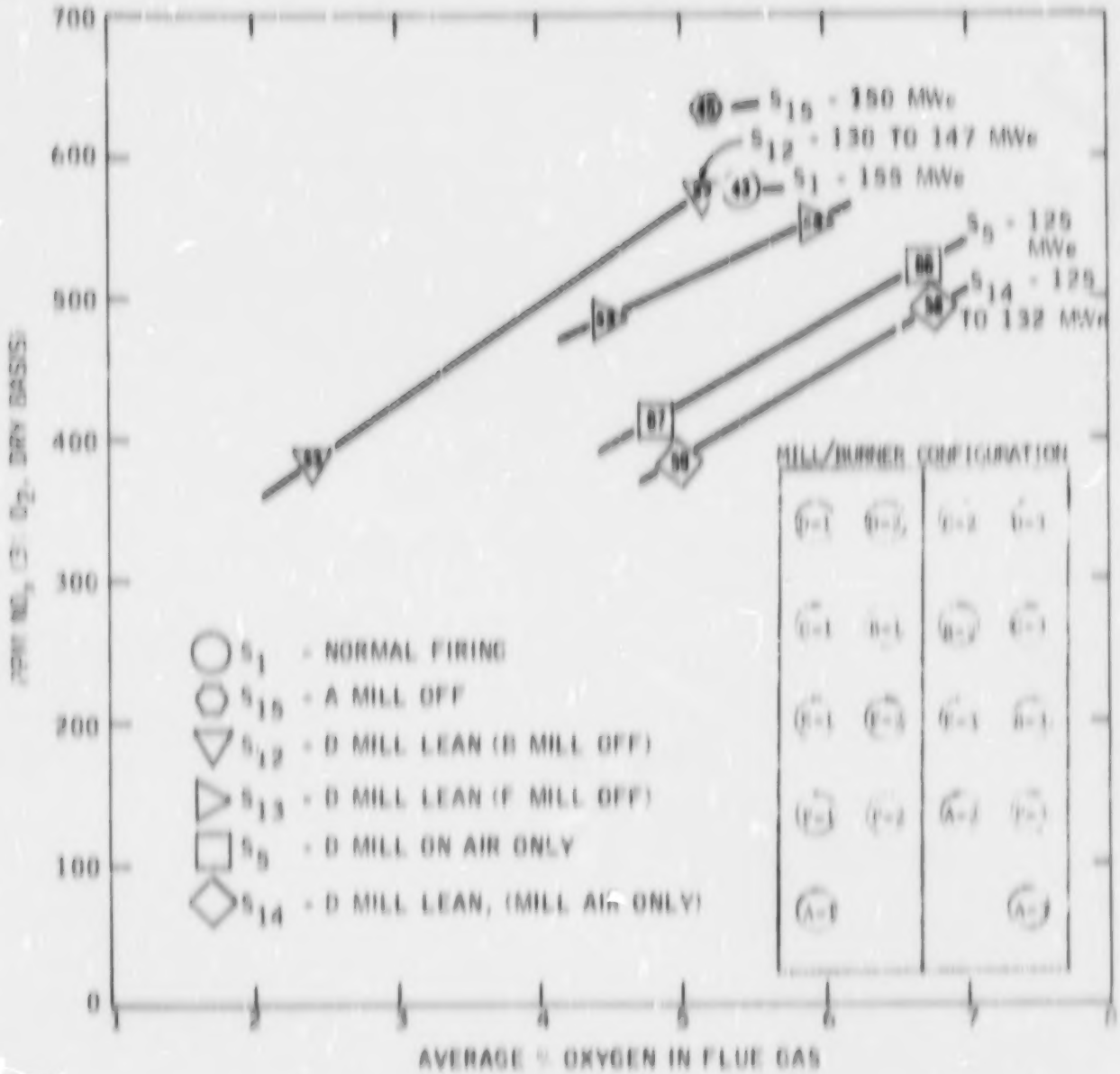


Figure 8. Effect of excess air and staging on NO$_x$ emissions (Sample No. 2 boiler - 123 to 155 MWe).

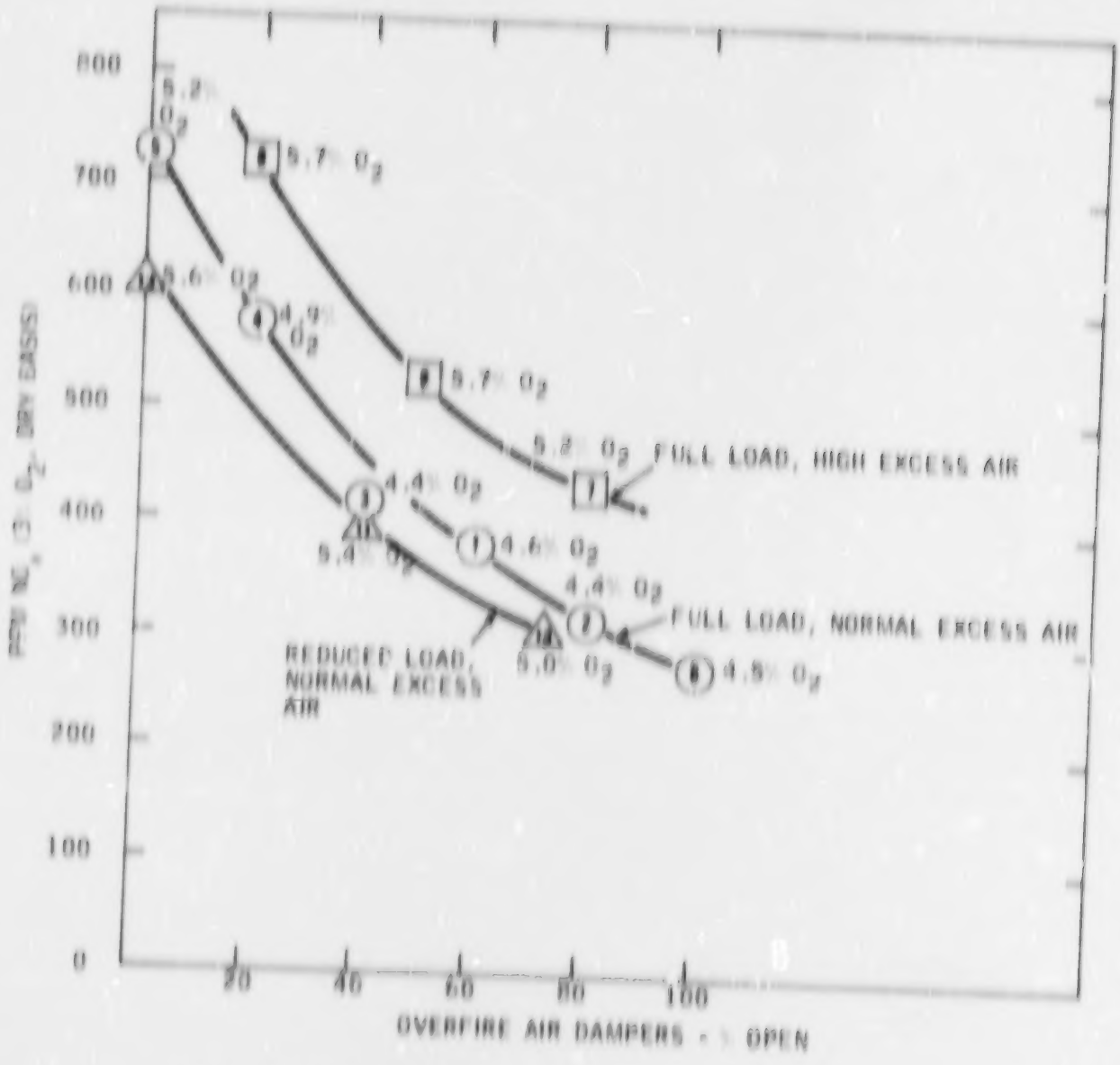


Figure 9. Effect of secondary air addition on NO_x emissions (Comanche No. 2 boiler - 275 to 355 MWE).

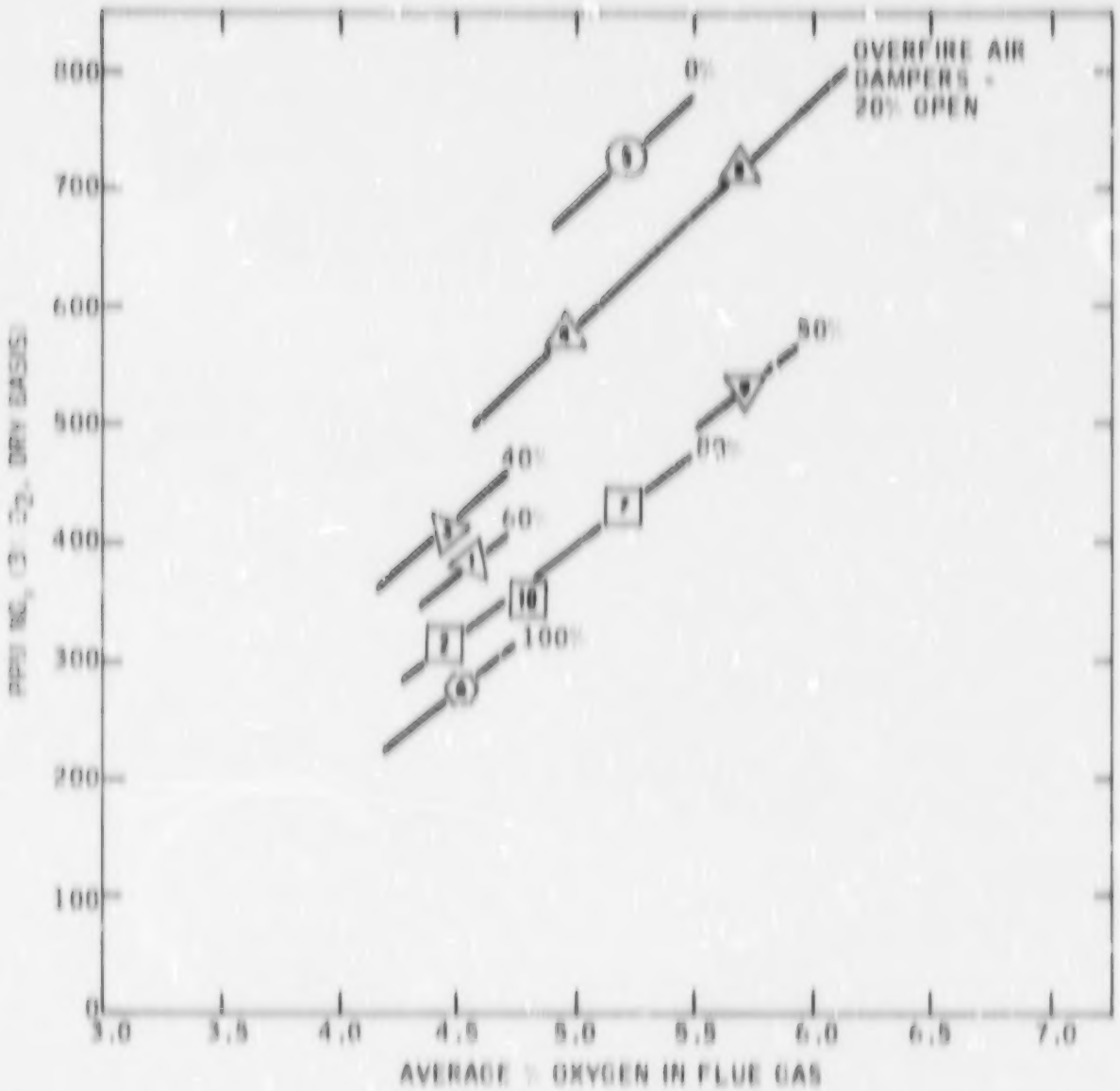
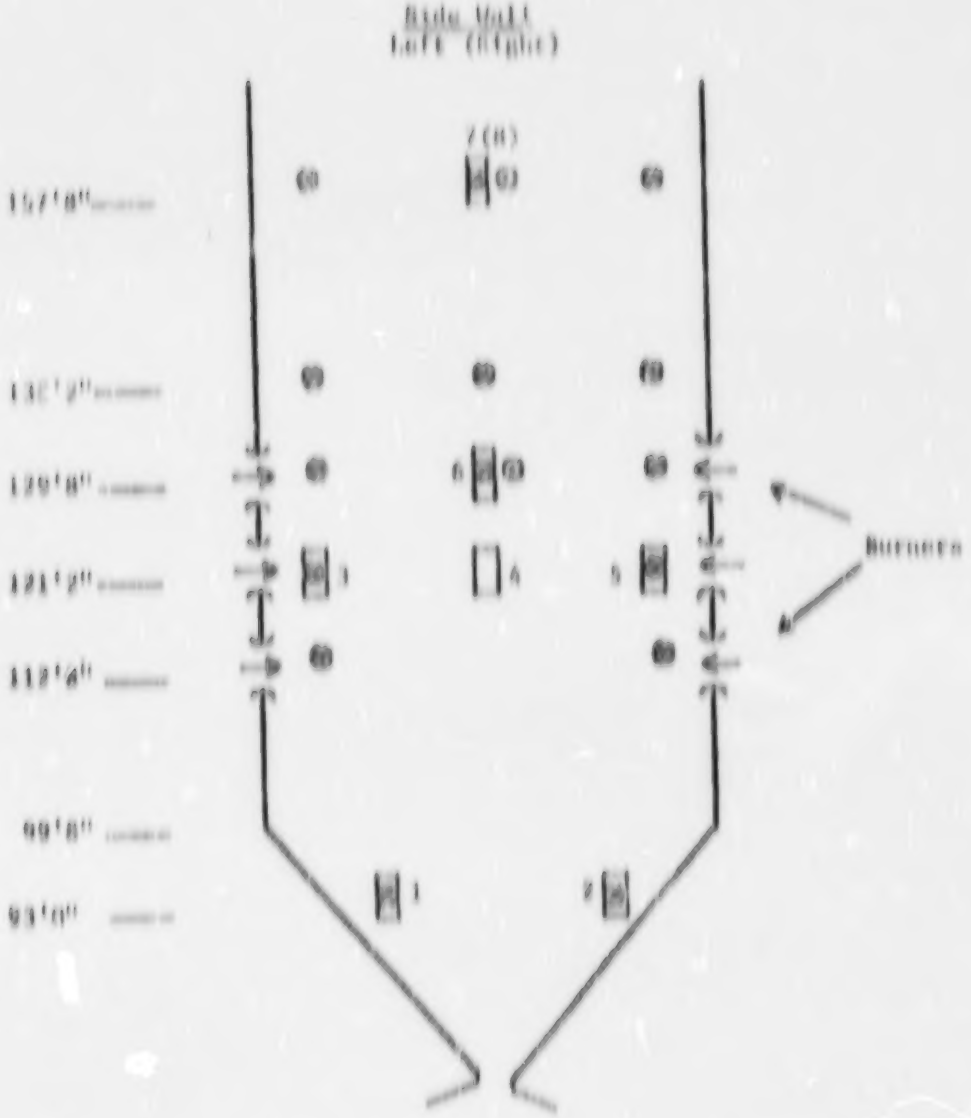


Figure 10. Effect of excess air in full load NO_x emissions (Comanche No. 2 boiler - at full load of operation).



[] Corrosion Test Panels

Ⓒ Corrosion Probes (Two Per Sidewall)

Ⓖ Furnace Gas Sampling Taps

Figure 11. Gulf Power - Crist station, No. 7
Corrosion panel locations.

ANALYSIS OF NO_x CONTROL IN STATIONARY SOURCES

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ABSTRACT

The subject program is a three-year effort to analyze NO_x control in utility boilers by combustion modifications. Results of a previous Aerospace Corporation study on this subject and those of the first year of the current study were presented two years ago at the first EPA Stationary Source Combustion Symposium. These studies concluded that there appeared to be no inherent limit to reduction in NO_x by combustion modification in utility boilers except those that may result from other undesirable side effects. Among those discussed were: (a) excessive water-wall erosion/corrosion, (b) excessive losses in plant efficiency, and (c) combustion instability. The first of these is being investigated experimentally by several agencies. The latter two were addressed during the past year in the Aerospace program and are the subject of this paper.

In general, the analysis of a large sample of data from tests on natural gas- and oil-fired utility boilers showed no significant effects on plant efficiency due to staged combustion (or burners-out-of-service) or the use of NO_x ports. The data available to this study were not adequate to evaluate this conclusion with respect to coal-fired boilers or for any other combustion modification technique (specifically, water injection or combustion air temperature control).

The analysis of combustion instability in utility boilers, however, did show that operating the burners fuel-rich (as in staged combustion) does tend to create more unstable combustion, specifically in air-side feed system-coupled modes of combustion instability. The fuel-rich burner operating conditions in staged combustion increase the dynamic response, or gain, of combustion in the furnace and the air flow rate through the burner. A method of analysis was developed which shows that, with proper design, these modes can be stabilized even with very fuel-rich burner operation.

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NOMENCLATURE

A_b	-	Cross-sectional flow area, for air, in a burner.
C	-	Capacitance within a burner.
$F_n(t)$ $(i=1-5)$	-	Arbitrary functions used to designate the furnace pseudo-acoustics, in five of the six directions.
$F(r)$	-	A function describing changes in local furnace pressures resulting from changes in the local combustion air/fuel ratio (through changes in the combustion temperature and molecular weight of the combustion products).
K_1	-	Constant describing damping during acoustic wave travel and the efficiency of wave reflection at solid boundaries.
L	-	Inertance of the air within a burner.
l_b	-	Length of a burner, in the flow direction.
M	-	Molecular weight.
P	-	Pressure; furnace (P_f); furnace response (P_{fo}); furnace input, or driving pressure (P_{fi}); constant windbox pressure ($\bar{P}_{wb}$).
R	-	Flow resistance; inlet to a burner (R_i); burner exit region (due to the presence of flame) (R_f); linearized (R_{if}, R_{ef}); linearized resistance to the flue gas flow from one burner in leaving the radiant section (exit) of the boiler (R_e); steady state resistance in the burner exit region due to the presence of a flame (R_f).
S	-	The LaPlace Operator.

T_1, T_2, T_3, T_4, T_{1a}, T_{2a} - Time constants in the expression for the dynamic response of a burner (equation (1)).

T - Temperature

a - The acoustic velocity in the air within a burner.

e - Designates an exponential term (natural).

g - The acceleration of gravity.

i - An index.

j - $\sqrt{-1}$

r - The weight air/fuel ratio.

$\dot{W}$ - Weight flow rate; air at the burner inlet ($\dot{W}_i$); air leaving the burner ($\dot{W}_b$); fuel leaving the burner (constant) ($\dot{W}_{fb}$); delayed burner flow rate ($\dot{W}_{bd}$); returning acoustic flow rates ($\dot{W}_{ar}$).

W_s - Weight of gases stored in the control volume in the furnace.

τ - Time delay; from the burner exit to the region of concentrated combustion (combustion time delay) at the steady-state burner flow velocity (τ_g); for acoustic wave travel from a burner exit to and from the exit from the radiant section of the furnace (τ_e); for acoustic waves travel from a burner exit to and from a solid boundary, in the (i) direction (τ_i).

ω - Frequency, in radians per second.

SUPERSCRIPT

- Time-invariant quantities.

SECTION I

INTRODUCTION

A paper was presented by the author two years ago at the first EPA Stationary Source Combustion Symposium that described Aerospace efforts to develop useful guidelines for the control of NO_x in natural gas-, oil-, and coal-fired utility boilers by combustion modifications (1). Fundamental to that effort was the use of large samples of NO_x and operational data from full-scale operating utility boilers. In general, results indicated no limits on NO_x reduction that could be considered inherent in the combustion modification techniques per se. Such limits would very likely result from the appearance of other undesirable side effects such as significant losses in plant efficiency, combustion instability, or water-wall erosion/corrosion. A number of activities/agencies have been examining the latter possibility. In the second year of an EPA grant, then, Aerospace undertook a study of the effects of combustion modifications made for the purpose of NO_x reduction on plant efficiency and combustion stability (2).

Overall plant efficiency data were available from the natural gas- and oil-fired utility boiler samples of previous NO_x control studies (3). These data showed efficiency losses of as much as 7 to 10 percent that, at least superficially, appeared to be related to lower NO_x levels. There would certainly be significant limits to NO_x reduction by combustion modification if such losses could be attributed to the NO_x control techniques.

Briefly, the study of plant efficiency showed that, at least within the limitations of the combustion modifications represented in available data sample, the NO_x control techniques caused no discernible changes in overall plant efficiency. The task to evaluate combustion instability, however, did show that, without proper design consideration, this could represent a significant limit on NO_x reduction by combustion modification. A method of analysis of air-side feed system coupled modes of combustion instability in utility boilers was developed showing that fuel-rich burner operation, as in

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the staged combustion technique, can lead to violent combustion instability. The analysis was verified by comparison with one (the only available) case of instability in a natural gas-fired utility boiler. The writer is aware of at least one case where combustion instability is currently limiting NO_x reduction in an oil-fired utility boiler to levels higher than current regulation.

Because the plant efficiency study results are rather straightforward whereas the combustion instability study shows a potential problem, and offers a solution, plant efficiency is discussed only briefly here and further discussion largely concerns the stability study.

Work has continued, at Aerospace, under EPA funding, on NO_x control methods beyond the efficiency and stability studies. This effort has concentrated largely on simplifying and improving the NO_x control model and in demonstrating application of results to utility boiler design for minimum NO_x within the bounds of high plant efficiency, combustion stability and low emissions of other air pollutants. Because this work is as yet incomplete, discussion of these results is also limited.

SECTION 2

CURRENT WORK

Studies just completed on NO_x control in utility boilers, under EPA funding, largely concerned simplification and improvements in the NO_x control analysis technique and demonstration of the use of the resulting guidelines. Major simplifications result from the observation, in previous Aerospace and other studies, that NO_x reduction by the staged combustion technique is nearly always greatest when the air-only burners and NO_x ports are all located above all of the active burners. For this reason, all burner configurations involving air-only burners below the top level of active burners (and the resulting enormous complexity of multiple and varied mixing zones throughout the furnace) were eliminated from further consideration. With this limitation the combustion product composition could be considered constant throughout the active burner region.

This limitation so greatly simplifies the active burner region that some of the simplifications and limitations of the previous NO_x control analyses could then be improved. It is now possible to directly integrate the NO_x formation rate equation along

flow paths through the active burner region and, with a small number of steps, through the zone where the remaining air is mixed in with the fuel-rich products from the active burner region. That limitation also allows better descriptions of combustion product cooling by radiation (proportional to the fourth power of the product temperatures) and finite gasification and initial mixing rates. While regression analysis of large samples of data from full-scale utility boilers is still used to quantify the resulting analysis, preliminary results indicate that NO_x levels calculated directly from the analysis are now much closer to measured levels than was previously possible. As of this writing, work in this area is continuing. Results will be published as an EPA report.

SECTION 3

PLANT EFFICIENCY

Briefly, the study of the effects of combustion modifications made for the purpose of NO_x reduction showed no distinguishable efficiency losses that could be attributed to the use of staged combustion (burners-out-of-service and/or NO_x ports). All of the efficiency losses that could be correlated in the data (up to 8 percent) appeared to result from load reduction. Although it is clear that NO_x does decrease with load (at least in the boilers in the data sample), load reduction is not considered a combustion modification for the purpose of NO_x control.

It is also clear, from the available data, that the combustion air temperature decreases with load. The observed NO_x reduction with load is very likely caused by the reduction in the combustion air temperatures. The loss in plant efficiency with load, however, appears to be primarily related to off-design operation of the steam turbines at reduced load. Thus the observed plant efficiency losses may not be related at all to the phenomena that cause the NO_x reduction. Unfortunately, there was insufficient data available to this study to directly evaluate the effects of combustion air temperature (or other combustion modification techniques such as water spray or flue gas dilution in the combustion air) on efficiency. Since these are considered potential NO_x control techniques, their effects on plant efficiency still need to be evaluated. Also, the data available to the previous study of coal-fired utility boilers (4) was not adequate to develop plant efficiency data.

SECTION 4

COMBUSTION STABILITY

Models and analysis techniques of feed system coupled modes of instability developed in the rocket industry were used as a basis for the development of a method of analysis for such feedback systems coupled to the air flow system in utility boilers. A major modification of these models and techniques was necessary to adequately describe the coupling between burner flow rate perturbations and resonances in the three coordinates of the furnace cavity. This modification complicated the analysis but it was shown that in the limiting case (primarily, in the case where the boiler cavity dimensions are very small) the analysis developed here becomes identical with that long used in the rocket industry.

Basically, the model can be described as follows. The boiler windbox is taken as a large, constant pressure plenum from which combustion air enters the burners. The air in the burners has compressibility and inertia. Resistance to air flow through the burner is in two parts, a constant resistance at the burner inlet (through the air registers) and a variable resistance near the burner exit that is a function of the degree of initial combustion within the burner.

In conventional utility boilers the pressure drop across the burners, from the windbox to the furnace, is very small, measured in inches of water. As a result, this pressure drop, and the resulting air flow rates, are quite sensitive to variations in furnace pressures at the burner exit. Small perturbations in furnace pressure at the burner exit cause large perturbations in the air flow rate through the burner. However, the pressure drop across the fuel injectors (or orifices) is usually quite large, measured in pounds per square inch (psi). Perturbations in furnace pressure, therefore, have small effects on fuel flow rates. As a result of constant fuel flow rates mixing with varying air flow rates, the air/fuel ratio leaving the burner is also varying. Figure 1 shows a model of the dynamics of air flow through a utility boiler.

The effect, in turn, of varying air flow rates and air/fuel ratios entering the furnace is in two parts. The total volume flow rate perturbations begin immediately upon leaving the burner to mix with the gases in the furnace, decelerating and generating

acoustic waves which propagate away in all six directions. The majority of the combustion takes place at some later time (the combustion time delay), further out in the furnace. Although the flow velocity perturbations have been damped out, the air/fuel ratio variations have not. Heat release rates, then, largely vary as a function only of the varying air/fuel ratio. When the burner is operating very fuel rich (a combustion modification for the purpose of NO_x control) the heat release rate varies strongly with air/fuel ratio. The varying heat release rates also create acoustic waves that propagate away in all six directions. Figure 2 shows a schematic of the dynamic coupling between the active burner flow and furnace pressure.

After appropriate time delays for acoustic wave travel to the limits of the furnace cavity, and reflection off of solid boundaries (at some efficiency), the waves return (at different times) to the burner exit and add together to create the furnace pressure variations that, in turn, cause further variations in air flow rates and air/fuel ratios coming out of the burner. Acoustic waves that travel to the exit of the radiant section of the boiler are partially dissipated as they cause varying rates of flow of gases out of the radiant section into the back pass.

Figure 3 shows a block diagram of a simple feed system coupled mode of combustion instability (called "chug") in a rocket engine (5). To apply such a model to a utility boiler using staged combustion for NO_x control, necessary major modifications include the effects of varying air/fuel ratio on the heat release and of acoustic phenomena in the large furnace cavity. Direct solution of the three-dimensional acoustic wave equation, coupled to the burner flows and including damping during wave travel and imperfect reflections from solid boundaries, introduces unnecessary complications in the analysis. Instead, a relatively simple set of "pseudo-acoustics" were developed that incorporate these phenomena in an analytically manageable form. The resulting block diagram is shown in Figure 4. The functions $F_n(t)$ account for acoustic wave travel in the six Cartesian coordinate directions, reflection off solid boundaries and return to their origin, with damping during wave travel. The model shown in Figure 4, when applied to the conditions of a chug mode of instability in a rocket engine, reduces to that schematically described in Figure 3.

The burner air flow response, developed from the model shown schematically in

Figure 1, is described analytically by the expression:

$$\frac{\dot{W}_b}{P_f} = \left(R_{1\ell}^{-1} + R_{1\ell}\right) \frac{1 + T_4 s + T_2^2 s^2}{1 + T_1 s + T_2^2 s^2 + T_3^3 s^3} \qquad (1)$$

where:

$$T_1 = \frac{R_{1\ell} R_{1\ell} C + L}{R_{1\ell} + R_{1\ell}}$$

$$T_2 = \left(\frac{1}{2} \quad LC\right)^{1/2}$$

$$T_3 = \left[\frac{1}{4} \quad \left(R_{1\ell}^{-2} C + R_{1\ell}\right)\right]^{1/3}$$

$$T_4 = R_{1\ell} C$$

$$L = \frac{L_b}{A_b R} \quad \text{(inertance)}$$

$$C = g \frac{A_b L_b}{a^2} \quad \text{(capacitance)}$$

$$R_{1\ell} = \left(R_1 \bar{W}_b\right) \quad \text{(inlet resistance)}$$

$$R_{1\ell} = \left(R_3 \bar{W}_b + \bar{W}_b \frac{dR_3}{d\bar{W}_b}\right) \quad \text{(exit, flame, resistance)}$$

Similarly, the response of the furnace pressure at the burner exit is described by:

$$\frac{P_f'}{W_b'} = R_b \frac{\left[\frac{1}{n}\sum_{j=1}^{n}\left(K_j e^{-\tau_j S}\right)\right]\left[1 + F(r)\frac{\bar{W}_b}{\bar{W}_{fb}} Se^{-\tau_c S}\right]}{e^{-\tau_b S} + \frac{\bar{W}_b R_{fb} - R}{P_f}} \qquad (2)$$

where:

$$F(r) = \frac{1}{T}\frac{dT}{dr} = \frac{1}{M}\frac{dM}{dr}$$

The overall, open looped response of an air-side feed system coupled mode of combustion instability in a utility boiler, as shown in the block diagram of Figure 4, is the product of Eqs. (1) and (2). To evaluate the frequency of this open loop the substitution

$$S = j\omega \qquad (3)$$

can be made. The system will be unstable, then, at those frequencies where the magnitude of the loop response is greater than one and the phase shift around the loop is 180 degrees (or $(2m-1)\pi$).

The only obvious observation which can be made directly from Eq. (1) is that the magnitude of the burner response can be reduced, and the overall loop made more stable, by increasing the steady-state resistance to air flow through the active burners, primarily by increasing the burner air inlet resistance, R_{fb}. (This is called "gain stabilization" (6).) It will be shown later that increased resistance due to the presence of partial combustion within the burner, R_{fb}, can have a strong destabilizing effect under some circumstances. This is particularly true if the flame is not firmly anchored in the burner exit and can move in and out of the burner as a result of (decreasing and increasing) air flow rate variations. The worst case of this, of course, is periodic flame lift-off.

Equation (2) shows a destabilizing effect of staged combustion, through the function F(r). This function represents the effect of air/fuel ratio variations on furnace pressure through the combustion heat release. With active burners operating at air/fuel ratios of the overall boiler, or near to stoichiometric, air/fuel ratio perturbations result in little or no pressure perturbations. The only destabilizing effect is that due to total flow rate variations. When an active burner is operated very fuel-rich (for purposes of NO_x control), however, small variations in the air/fuel ratio of the mixture leaving the burner cause large variations in the heat release in combustion (F'(r) is large) and subsequent large furnace pressure variations. In the extreme case, where the steady-state burner air/fuel ratio is near the fuel-rich flammable limit, the flame could alternately lift-off of, and flash back to the burner exit. In this case the function F(r) is essentially infinite and violent instabilities should result.

Some of the more significant results of more detailed calculations of the magnitude of the open loop response (stability) as a function of frequency are shown in the remaining figures. Figure 5 shows a comparison of this calculation (for a full-scale, natural gas-fired utility boiler), using Eqs. (1) and (2) of this analysis and developed from the model shown in Figure 4, with the simple rocket engine analysis described by the model shown in Figure 3. The agreement is good except that this analysis introduces the effects of the furnace cavity resonances and the low frequency stabilizing effect of the steady-state resistance of partial combustion within the burner.

Figure 5 also shows that the intermediate peaks of response are not at the resonant frequencies of the furnace cavity, as might be expected, but are between these resonances. This is because the burner air flow rate response is 180 degrees out-of-phase with the furnace pressure at the burner exit (the minus sign in Eq. (1)) and a strong resonance tends to damp burner flow rate oscillations.

Figure 6 shows a comparison of results of this analysis with experimental observations from the single case of instability in a full-scale (natural gas-fired) utility boiler available to this study. The instability frequencies predicted by this analysis are shown by the circles drawn on the response curves (the frequencies where the open loop phase shift is 180 degrees). Unstable operation is predicted where the magnitude of the open loop response is greater than one at the frequencies noted by the circles. The

response curves shown are for an active burner located at the bottom of the burner array. Because the appropriate value of the combustion time delay is not well-known, Figure 6 shows the response curves for each of three values of this time delay.

The degree of agreement is considered reasonably good. A strong instability is predicted at 10 to 11 hertz and a strong instability was observed at about 12.5 hertz.

The analysis shown in Figure 6 implies a possible instability in the 27 to 35 hertz range, but none was observed. Although not shown in this paper, response curves similar to those shown in Figure 6 for burners higher up in the active burner array show that the overall response of the total burner array would be soundly stable in this frequency range.

The response curves shown in Figure 6 indicate a potentially unstable mode in the 43 to 45 hertz range. It seems clear that slightly different modeling assumptions or input constants could show a possible weak instability in this frequency range. Mild oscillations were observed in the 40 to 50 hertz range which appeared and disappeared as operating conditions changed.

Figures 7 and 8 show the two effects discussed earlier relative to Eqs. (1) and (2). Figure 7 shows the effects of a poorly anchored flame within an active burner. The numbers, n, with which the curves are labeled essentially represent the sensitivity of the fraction of combustion completed within a burner to variations in the air flow rate through the burner. A value of (n=0) represents a solidly anchored flame, with the fraction of combustion completed within the burner independent of air flow rate variations. In this case, the presence of partial combustion within the burner has a stabilizing effect, resulting from the increased steady-state resistance to air flow through the burner. Not shown in Figure 7 is another possible curve, for (n = infinity). This represents the case where the flame is so poorly anchored that, in response to air flow rate variations, it alternates between positions deep within the burner and completely lifted off the burner exit. Such a case could be violently unstable.

Figure (8) shows the effect of staged combustion on stability. As the fuel is cut off to more burners (more air-only burners in the total burner array), the open loop response at the (lowest) unstable frequency becomes larger. Near the fuel-rich flammable limit in the burner the case of alternate lift-off and flash-back can be

encountered and again the system can become violently unstable.

The violent instabilities which can accompany both of these cases can be avoided by careful attention to burner design to provide: (a) soundly steady flame anchoring within or just downstream of the burner exit; and (b) local air/gaseous fuel ratios in the flame issuing from the burner, which are maintained well above the fuel-rich flammable limit until combustion is nearly complete. Combustion instability can represent a significant limit to NO_x reduction by the staged combustion technique unless this attention is paid to burner design.

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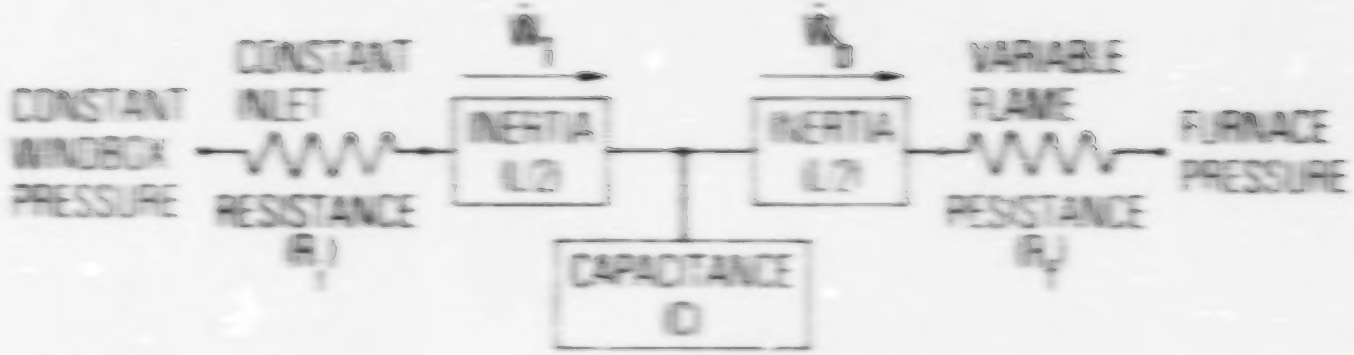


Figure 1. Model of the dynamics of a burner in a utility boiler.

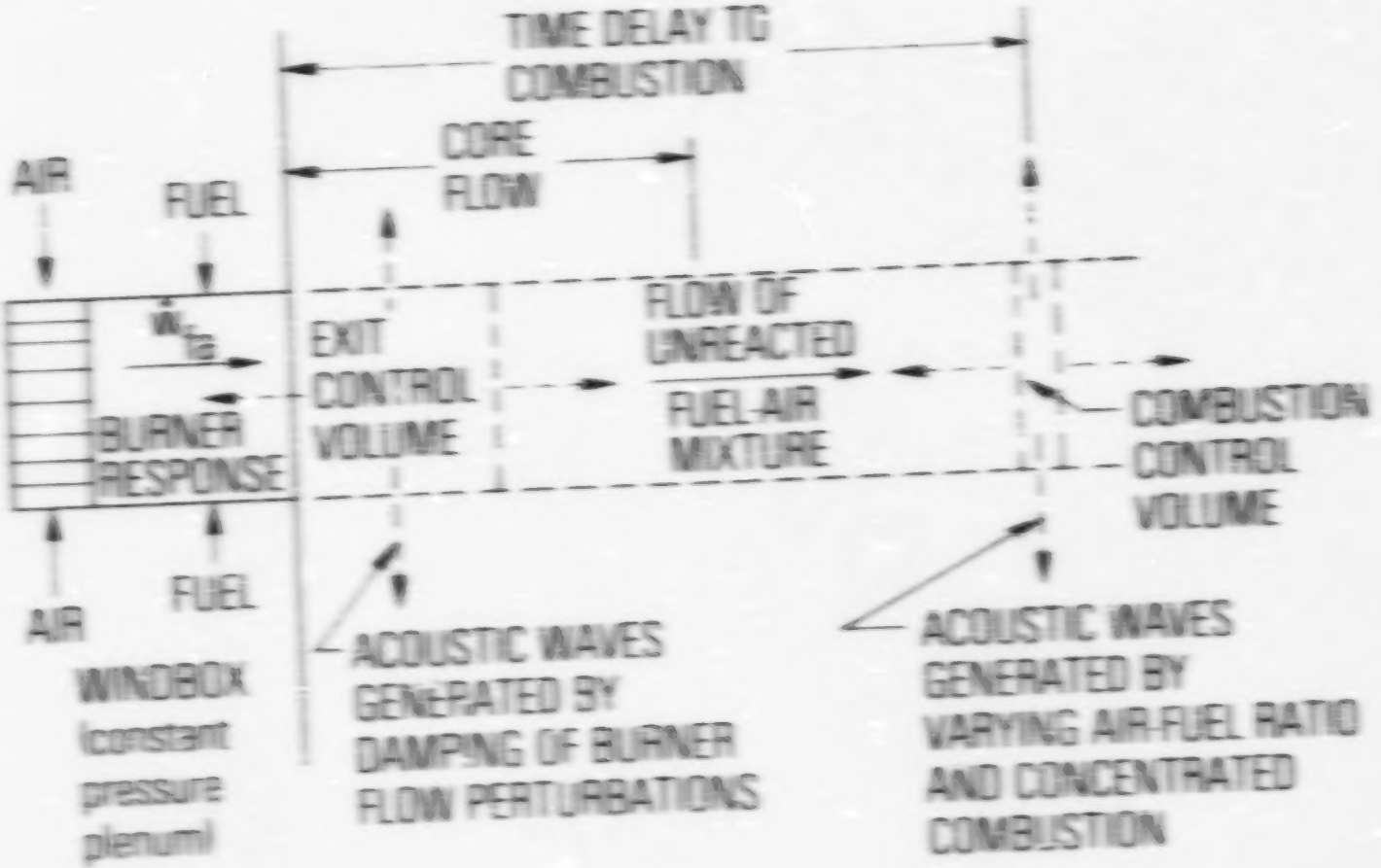


Figure 2. Active burner flow and combustion model.

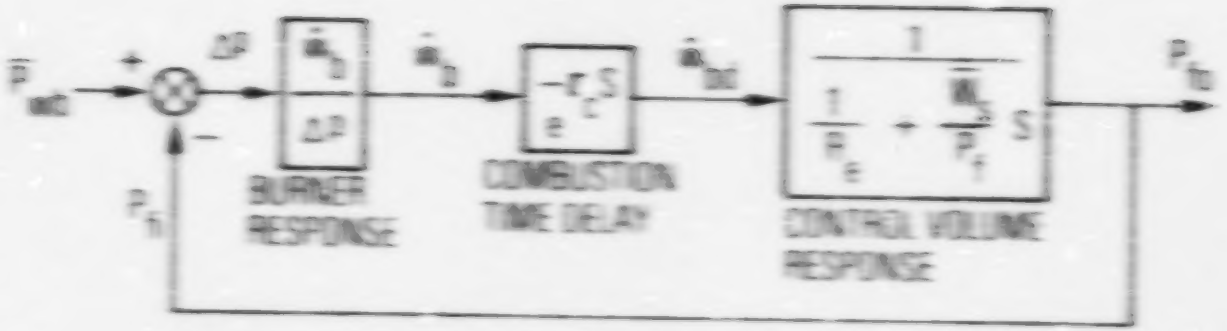
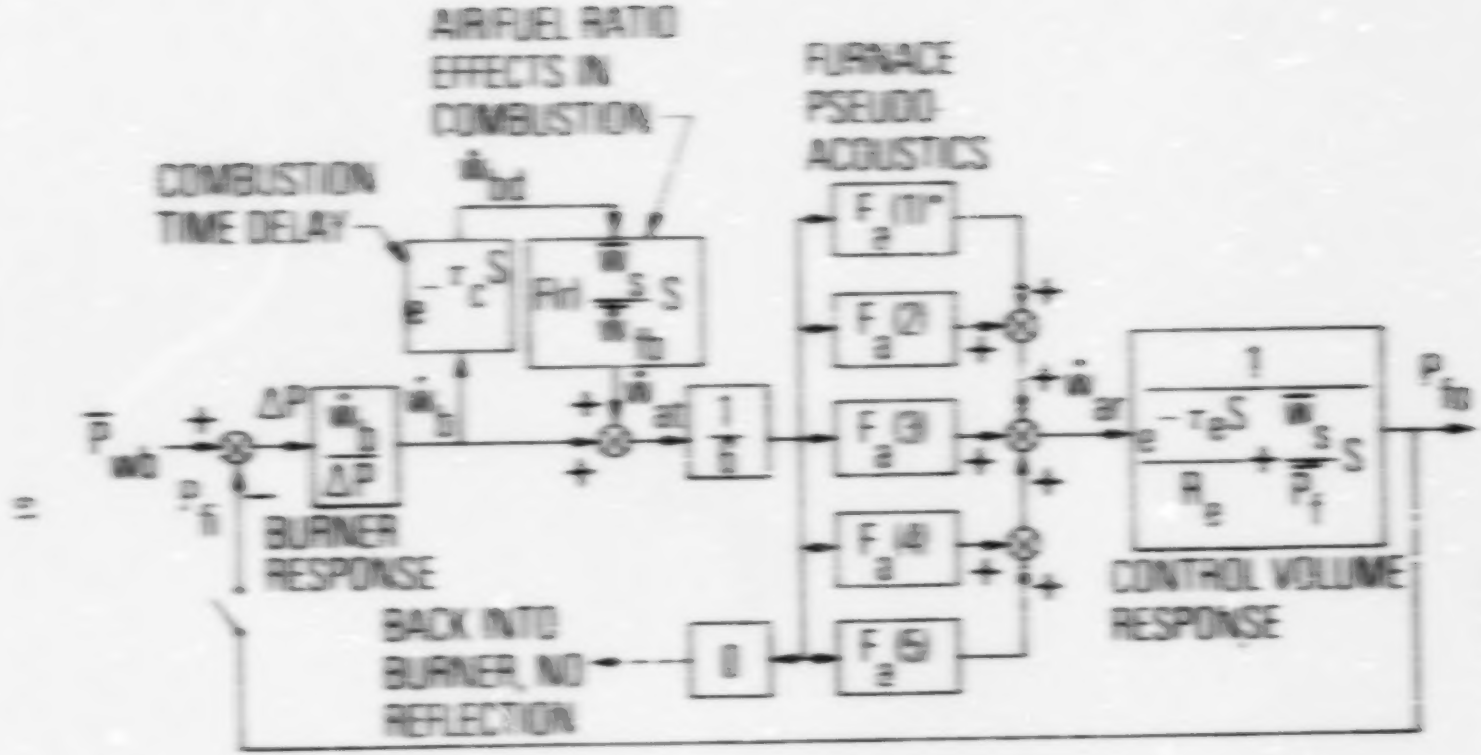


Figure 1. Typical liquid rocket engine model of a low frequency (chug) feed system coupled mode of combustion instability (simplified from Figure 4).



$$*F_a(j) = K_j e^{-\tau_j S}$$

Figure 4. Model of an air feed system coupled mode of combustion instability in a utility boiler.

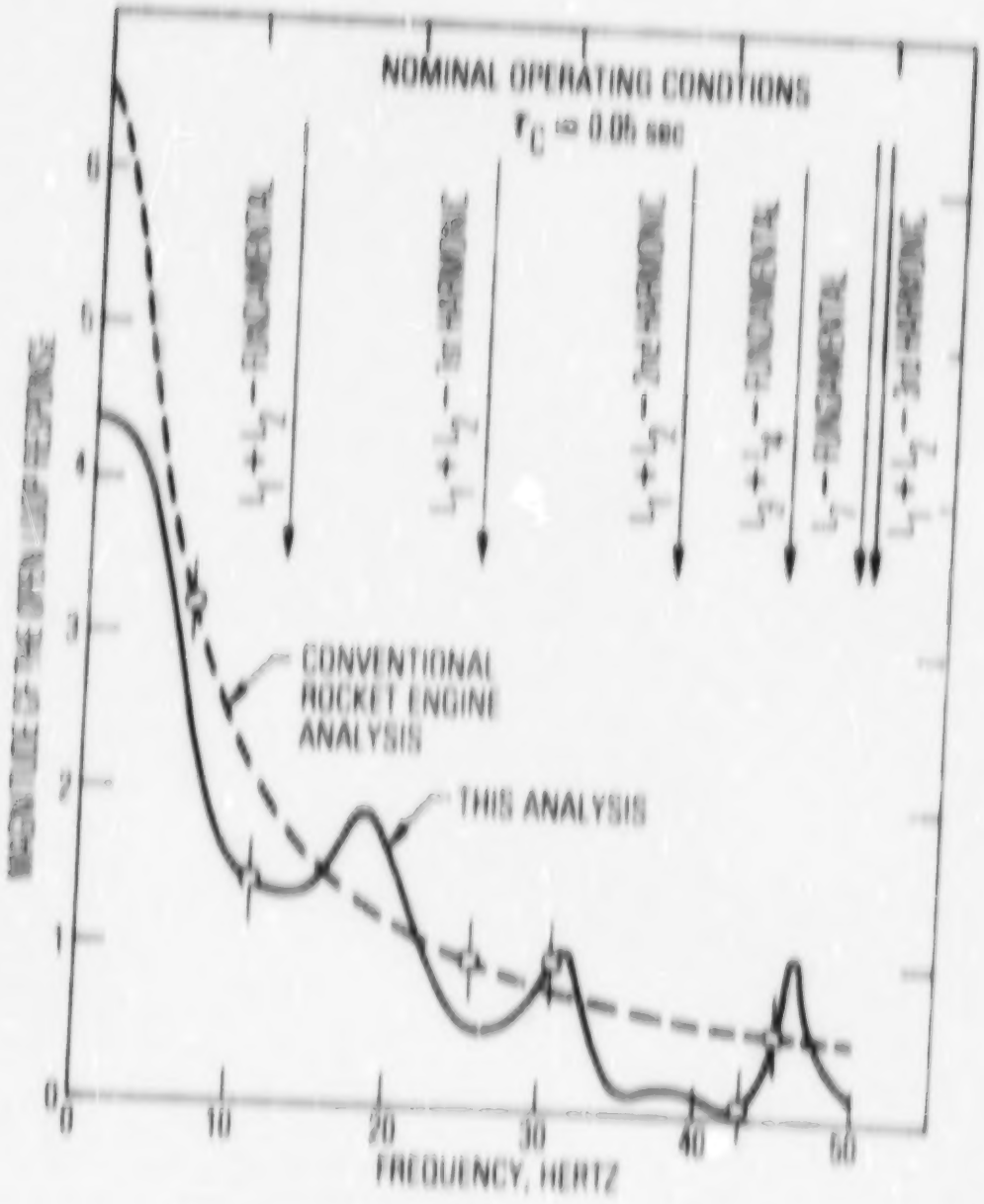


Figure 5. Comparison of results of the current analysis with those of conventional rocket engine analysis.

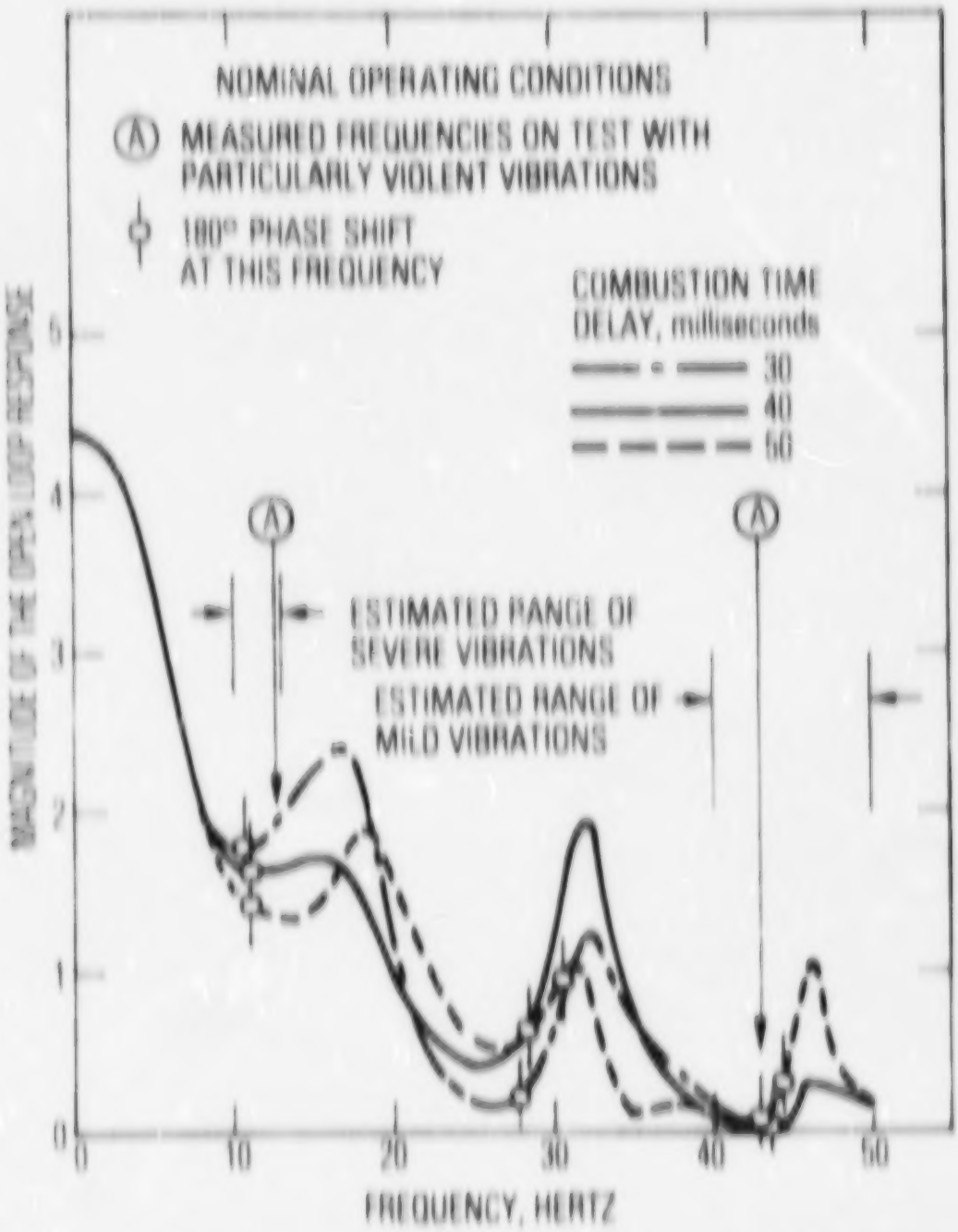


Figure 6. Comparison of analytical predictions with experimental observations.

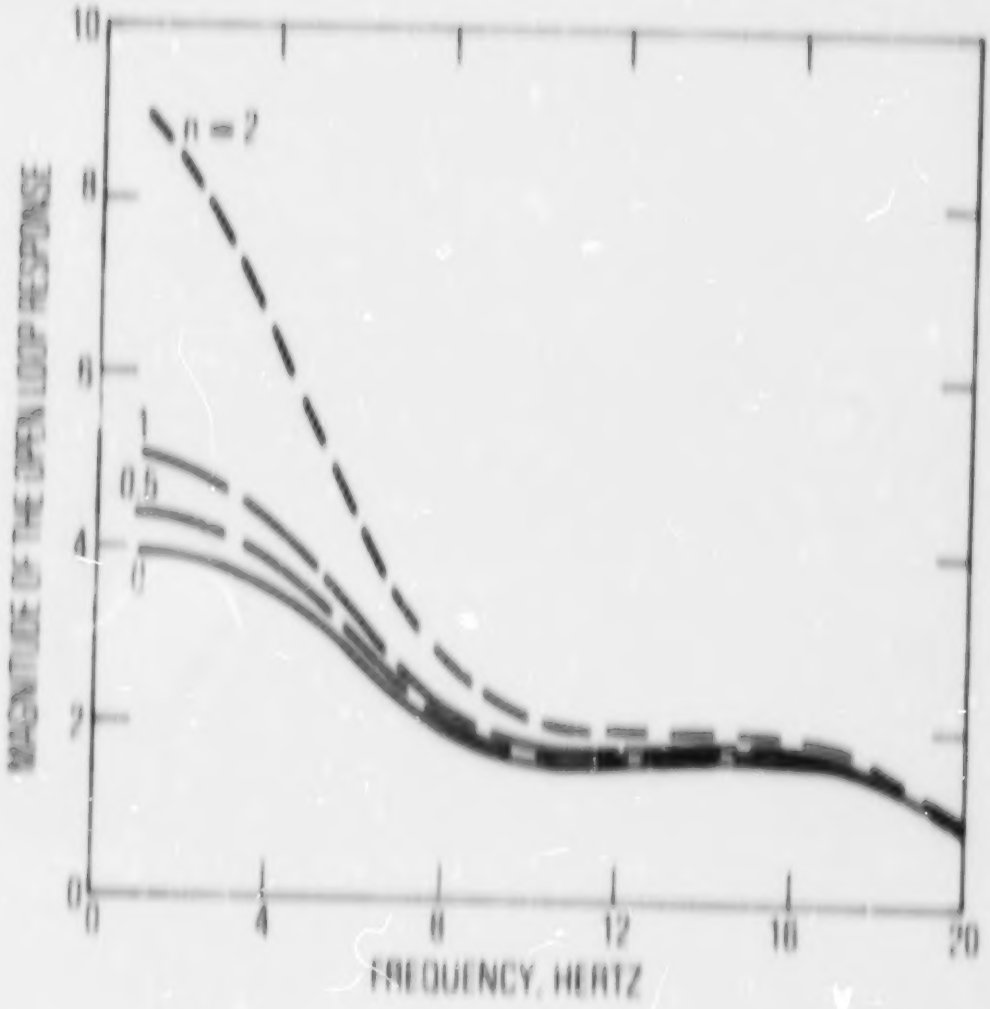


Figure 7. Effects of the fraction of combustion completed within an active burner on combustion stability.

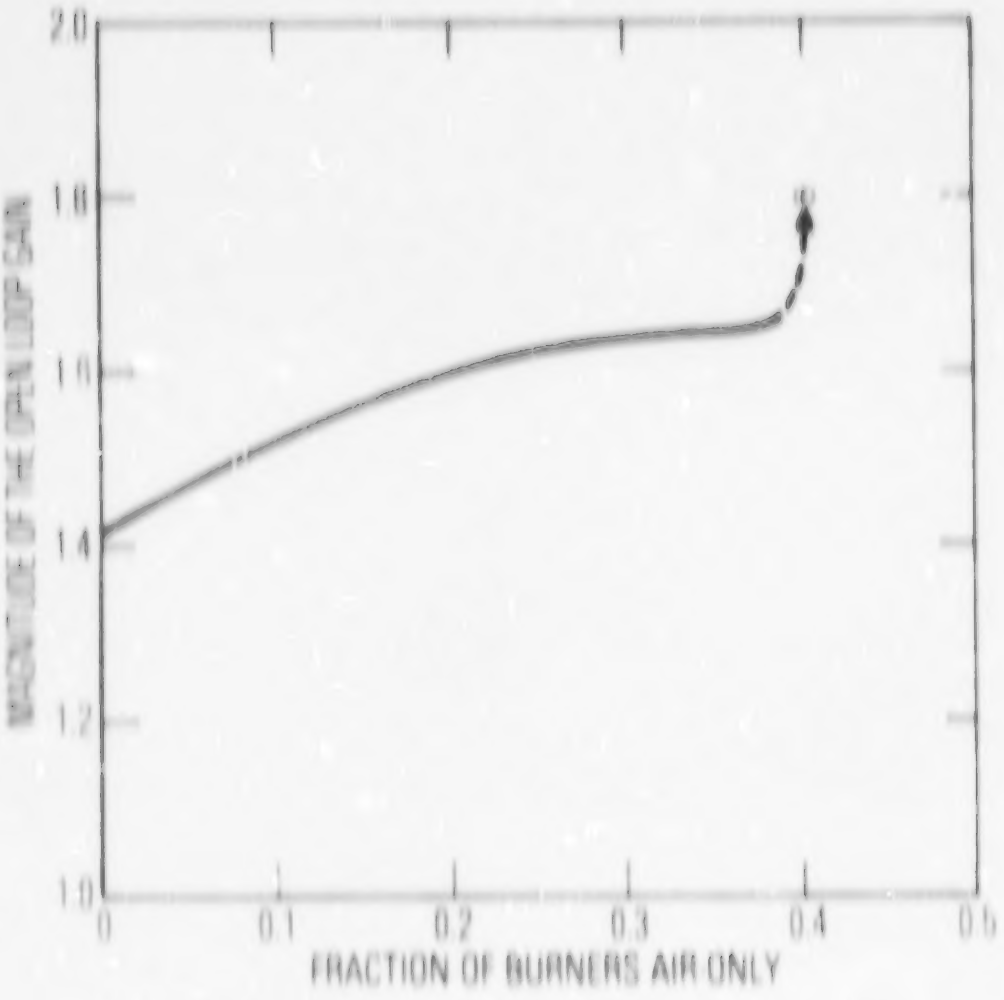


Figure 8. Effects of the degree of burners-out-of-service on instability at the unstable frequency.

OVERFIRE AIR TECHNOLOGY FOR TANGENTIALLY FIRED UTILITY BOILERS BURNING WESTERN U.S. COAL

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ABSTRACT

The paper reviews the results of a program designed to study methods of reducing NO_x formation in tangentially fired steam generating units firing western U.S. coal types. High (western bituminous) and low (sub-bituminous) rank coals were studied. This program was performed under the sponsorship of the Office of Research and Development of the Environmental Protection Agency (Contract 68-02-1486).

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CONVERSION FACTORS

SI METRIC UNITS TO ENGLISH UNITS

To Convert From	To	Multiply By
kg/s	10^3 lb/hr	7.936640
ng/J	lb/10^6 Btu	2.326E-3
MJ/s	10^6 Btu/hr	3.412141
ug/J	lb/10^6 Btu	2.326
J/g	Btu/lb	4.299226E-1
MN/m^2	PSIA	1.450377E+2
kW/m^2	10^6 Btu/hr-ft^2	3.169983E-1

ENGLISH UNITS TO SI METRIC UNITS

To Convert From	To	Multiply By
10^3 lb/hr	kg/s	1.259979E-01
PSIA	MN/m^2	6.894757E-3
lb/10^6 Btu	ng/J	4.299226E2
lb/10^6 Btu	ug/J	4.299226E-1
10^6 Btu/hr	MJ/s	2.930711E-1
Btu/lb	J/g	2.326
10^6 Btu/hr-ft^2	kW/m^2	3.154590

$^{o}F = 1.8\ (^{o}C) + 32^{o}$

ABBREVIATIONS AND SYMBOLS

Abbreviations	Definitions
NO_x	Oxides of Nitrogen
THC	Total Hydrocarbons
NA	Not Available
X-S	Excess
WW	Waterwall
MCR	Maximum Continuous Rating
TA	Theoretical Air to Fuel Firing Zone
EA	Excess Air
FFZ	Fuel Firing Zone
NSPS	New Source Performance Standard

Symbols	
NO_2	Nitrogen Dioxide
CO	Carbon Monoxide
O_2	Oxygen
SO_2	Sulfur Dioxide
CO_2	Carbon Dioxide

Note: % TA = Percent theoretical air to the active fuel firing zone. 100% TA equals stoichiometric air required for combustion.

EA = Percent excess air measured at the economizer outlet (with no overfire air 115% TA = 15% EA_1 with overfire air 105% TA + 10% OFA = 15% EA).

INTRODUCTION

The emphasis on improved quality of the environment has led to the design of coal-fired steam generators with overfire air equipment to reduce and control NO_x emission levels. In tangentially-fired steam generators, the overfire air is admitted through registers in an extended windbox.

Tests conducted on Combustion Engineering coal-fired steam generators have demonstrated that overfire air with tangential firing has been effective in reducing NO_x emission levels by as much as 50 percent of uncontrolled values.

Some of the field tests were performed by Combustion Engineering, Inc. under an Environmental Protection Agency sponsored two-phase program to identify, develop, and recommend the most promising combustion modification techniques for the reduction of NO_x emissions from tangentially coal-fired utility boilers with a minimum impact on unit performance.

The previous two-phase program is briefly described as follows:

Phase I (EPA Contract 68-02-0286) consisted of the selection of a suitable utility boiler to be modified for experimental studies to evaluate NO_x emission control, and a preliminary application economic study indicating the cost range of a variety of combustion modification techniques applicable to existing and new boilers [1].

Phase II (EPA Contract 68-02-1467) consisted of modifying and testing the utility boiler selected in Phase I to evaluate overfire air and biased firing as methods for NO_x control. This phase also included:

1. The completion of detailed fabrication and erection drawings;
2. Installation of analytical test equipment;
3. Updating of the preliminary test program.

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4. A baseline operation study.
5. Analysis and reporting of test results.
6. The development of control technology application guidelines for existing and new tangentially coal-fired utility boilers.

This program was conducted at the Barry Steam Station, Unit No. 2 of the Alabama Power Company [2,3].

The major portion of the early EPE test programs, and those completed for EPA were conducted on units firing Eastern or Midwestern bituminous coals.

In recent years, the utilization of low sulfur Western U.S. coals as an energy source has increased significantly. The incentive for their use is the capability of meeting NO_x emission levels without the use of flue gas scrubbers. These fuels are abundant and may be used in lieu of oil and natural gas, which are in short supply.

Following the Phase II tests for EPA, a recommendation was made to investigate Western coal types for NO_x emissions. A contract (EPA Contract 68-02-1386) was awarded to Combustion Engineering, Inc. to field test a Western bituminous coal and a Western subbituminous coal.

The objective of this program was to investigate the effectiveness of employing overfire air as a method of reducing NO_x emission levels from tangentially fired steam generators firing Western U.S. coals. The effect of reducing NO_x emission levels was evaluated with respect to unit performance, unit efficiency, waterwall corrosion rates, and related gaseous emission levels.

Specifically, the factors considered in realizing this objective were as follows:

1. The program was conducted on two steam generating units designed with overfire air registers, the first unit firing a Western U.S. subbituminous coal and the second unit firing a Western U.S. bituminous coal.
2. The test program evaluated baseline, biased firing, and overfire air operation and consisted of approximately 60 steady-state tests per unit averaging two to three tests per day and two months of waterwall corrosion rate studies per unit.
3. The effect of NO_x control methods on all gaseous constituents

was evaluated during all tests. The following constituents were measured: NO_x, SO_x, CO, THC, O_2 and particulate samples for unburned combustible analysis.

4. The effects of NO_x control methods on steam generator performance were evaluated during all tests by obtaining necessary temperatures, pressures, flows, etc., with calibrated equipment.
5. Based on the results of this program, conclusions and recommendations were made pertaining to the acceptable application of staged firing with respect to NO_x emission levels, corrosion rates, and unit operation for each type of coal tested.
6. The results of this program were compared with the results obtained under Contract 68-02-1167 for a unit equipped with an overfire air system not included in the original design.

This paper will report major results of the Western coal test program conducted at Utah Power and Light Company's Huntington Canyon No. 2 unit and Wisconsin Power and Light Company's Columbia No. 1 unit. Additionally, major results from Alabama Power Company's Barry No. 2 unit are reported, so that results from all three units can be readily compared.

Side elevations of the three test units are shown in Figures 1, 2, and 3. Major design features of the test units are presented in Table I, and average coal properties are given in Table II.

OVERFIRE AIR SYSTEM DESIGN

The overfire air (OFA) system (Fig. 4) retrofitted to the Barry Unit No. 2 provided for the introduction of up to 20 percent of the total combustion air above the fuel admission nozzles at full unit loading. The overfire air was introduced into the furnace tangentially through two separate compartments near each furnace corner located approximately 2.4 meters above the fuel admission zone.

While the Barry Unit No. 2 required separate OFA compartments due to unit structural considerations, the Huntington Canyon No. 2 and Columbia No. 1 OFA systems (Fig. 5) were designed as vertical extensions of the corner windboxes.

All three systems provided for fuel/air and OFA nozzle tilting (± 30 degrees from vertical plane) and separate compartment flow control dampers to permit a study of the effects of various flow rates, introduction angles, and compartment airflow distributions.

TEST INSTRUMENTATION

The effect of using overfire air as a combustion process modification technique for emissions control was evaluated using the following instrumentation (Figure 6) and methods.

1. A Scott chemiluminescence NO-NO_x analyzer (0-2000 PPM).
2. An L&N paramagnetic O_2 analyzer (0-25 percent).
3. A Beckman non-dispersive infrared CO analyzer (0-1000 PPM).
4. A Scott flame ionization total hydrocarbon (THC) analyzer (0-1000 PPM).
5. ASME particulate train and ASTM carbon analysis.

Unit performance was monitored using the instrumentation and analytical procedures shown in Table III.

RESULTS

BASELINE OPERATION STUDY

It has been well documented that the formation of NO_x is dependent upon excess air and the oxygen concentration in the combustion zone, the oxygen concentration in the combustion zone being directly related to excess air and also to the theoretical air (TA) in the fuel firing zone. Theoretical air to the fuel firing zone is a computational tool used by Combustion Engineering, Inc. that accounts for variations in position and leakage to all windbox compartment dampers. This method allows for the accounting of leakage in the compartments above the top active fuel compartment and, therefore, is a better approximation of the actual air (i.e., oxygen available for combustion in the fuel firing zone than is total excess air (EA). Therefore, all parameters are plotted versus theoretical air to the fuel firing zone, rather than the total excess air. For the baseline operation study, the TA is essentially the same as the total excess air measured at the economizer outlet.

Figure 7 is a plot of NO_x* versus TA for the full load baseline tests at Alabama Power Company's Barry Station Unit No. 3, Utah Power and Light Company's Huntington Canyon Station Unit No. 2 and Wisconsin Power and Light Company's Columbia Energy Center Unit No. 1. As shown by this figure, NO_x is proportional to TA and, therefore, to oxygen concentration in the fuel firing zone and excess air.

Figure 8 is a plot of NO_x versus TA for the half load tests for all three units. As with the full load tests, the half load tests also show increasing

* Throughout this paper, oxides of nitrogen (NO_x) are expressed as nitrogen dioxide (NO_2) to be consistent with the reporting requirement of the Standards of Performance for New Stationary Sources (5).

NO_x emission levels with increasing TA. Comparison of the full and half load tests show that at similar theoretical air levels, the NO_x emission levels for the half load tests are lower or equal to the NO_x levels for the full load tests. The effect of load is better shown in Figure 9, where NO_x emission levels are plotted against theoretical air level for full, three quarter, and one half load baseline tests. This plot shows that in some, but not all cases, NO_x levels tend to increase with unit loading. It can also be shown that occasionally the opposite trend was observed. While NO_x levels correlated well with TA, attempts to find what effect fuel nozzle tilt and furnace condition had on NO_x formation were not as successful. The effect of fuel nozzle tilt was found to have a wide and inconsistent variation with NO_x emission levels.

Other investigators have found that increased slagging of the furnace walls tend to increase NO_x by increasing the furnace outlet temperature and, therefore, the bulk flame temperature (5,6). Bulk flame temperature increases due to the reduced heat transfer from the hot combustion gases to the water-cooled furnace walls. The amount of reduction in heat transfer may depend greatly upon the type of slag on the furnace walls. The furnace conditions for the full and half load tests are indicated on Figures 7 and 8. Furnace condition showed no discernable effect on NO_x emission levels. Furnace condition was measured by visual observation of the furnace waterwalls. Since waterwall absorption is closely related to furnace condition, an attempt was made to correlate NO_x emission levels with furnace waterwall absorption and therefore with furnace condition. This attempt produced no meaningful results. The lack of correlation between NO_x emission levels and furnace condition may be partially attributed to the fact that the visual observation of furnace waterwall deposits is very subjective.

The effect of reducing TA on CO emission levels and carbon heat loss is shown on Figures 10 and 11 for the full load tests. Both CO emission levels and carbon heat loss increase with decreasing TA. This trend is a result of the reduced oxygen available for complete combustion. CO emission levels show no effect due to furnace condition. However, carbon heat loss appears to decrease with increasing furnace waterwall deposits. This may be related to the higher bulk flame temperatures encountered in a heavily slagged furnace.

accomplished by changing the overfire air register damper opening. The maximum overfire air rate corresponds to the overfire air register dampers being 100 percent open. With the exception of Barry No. 2, the overfire air systems were designed to introduce up to 15 percent of the total combustion air above the top level of fuel nozzles at MCR. Barry No. 2 was designed to introduce 20 percent of the total air as overfire air. During normal boiler operation, the overfire air dampers are opened just enough to cool the overfire air registers.

As the overfire air dampers are opened, the NO_2 emission levels drop for a constant excess air level. This trend is shown in Figure 14. Six excess air levels have been shown, with the trend being similar for all excess air levels.

Theoretical air to the fuel firing zone and overfire air damper opening are closely related, with TA decreasing as the overfire air damper opening increases. Figure 15 is a plot of NO_2 versus TA for the damper variation tests for all three units. For these tests, as in the baseline and biased firing studies, the NO_2 emission levels are found to increase with increasing TA. The evidence shown in Figures 13 and 15 indicates that NO_2 is more dependent upon TA rather than EA.

Once the optimum excess air level and overfire air rate had been determined for each unit, the second test series was run. This test series involved a variation in tilt of the overfire air registers and fuel nozzles. The variation in tilt refers to how many degrees toward or away from each other the fuel nozzles and overfire air registers are moved. This variation is calculated by taking the difference in degrees that the overfire air registers are angled toward or away from the fuel nozzles, i.e., overfire air register tilt minus fuel nozzle tilt.

Tilt variation of the fuel nozzles and overfire air registers is designed to move the fuel firing zone both in the furnace and in its position relative to the overfire air registers. Movement of the fuel nozzles and overfire air registers away from each other accentuates the effect of staged combustion. Movement of the fuel nozzles and overfire air registers toward each other minimizes the effect of staged combustion because the air is being forced down into the firing zone.

BIASED FIRING OPERATION STUDY

Biased firing involves the removal of a fuel firing elevation from service with the dampers left open to admit air through the idle fuel nozzle elevations. The effect on NO_2 emission levels when taking various fuel elevations out of service is shown in Figure 12. The lowest NO_2 levels for each unit were obtained when the top fuel firing elevations were removed from service and the respective compartment air dampers were 100 percent open. Overfire air operation is simulated by this method of unit operation. The trend is for increased NO_2 levels as the elevation being removed is lower in the windbox. The increase in NO_2 levels can be attributed to the increased oxygen available in the fuel firing zone.

Examination of the units on an individual basis showed a slight reduction in NO_2 levels when the bottom fuel firing elevation was removed from service. This reduction in NO_2 might be caused by a cooling of the hot combustion gases by the cooler combustion air being admitted through the bottom fuel firing elevation.

In Figure 13, NO_2 is plotted versus TA for the full load biased firing tests. The correlation found for the baseline tests is also evident for the biased firing tests, NO_2 being directly proportional to TA.

CO emission level and carbon heat loss plots for the biased firing tests have not been included. Preliminary plots of these variables against TA revealed wide and inconsistent variations. This inconsistency is most probably due to firing with different fuel elevations out of service.

OVERFIRE AIR OPERATION STUDY

The overfire air operation studies were divided into three separate test series, each designed to determine an optimum operating condition. The three test series were:

1. Excess air and overfire air rate variation
2. Overfire air register tilt variation
3. Load and furnace waterwall deposit variation at optimum conditions

The first of these test series involved the variation of the overfire air rate at various excess air levels. Variation of the overfire air rate is

Figure 16 is a plot of NO_x versus the difference in tilt of the fuel nozzles and overfire air registers. NO_x emission levels are found to be highest when the overfire air registers and fuel nozzles are angled toward each other and lowest when they are angled away from each other. From the standpoint of NO_x reduction, the optimum tilt orientation would be with the overfire air registers and fuel nozzles angled away from each other. However for ease of boiler operation, parallel operation of the overfire air registers and fuel nozzles would be best.

In Figure 17, NO_x is plotted versus FA for the second series of tests in the overfire air mode. Again, NO_x emission levels are found to be directly proportional to FA.

In the final series of tests for each unit, the effects of load and furnace waterwall recycle on NO_x formation are examined. Boiler operation was at the optimum conditions determined in the previous test series for each unit. Mill, three-quarter, and full load tests were conducted on each unit at clean and dirty furnace conditions. Figure 18 is a plot of the NO_x emission levels versus FA for each test in this series. This figure attempts to minimize the effect of FA and show the effect of load and furnace condition on NO_x emission levels. Both Huntington No. 2 and Kimberly No. 1 show increases in NO_x levels as unit load rises from half load to full load. The effect of furnace condition on these units shows inconsistent variation in the results except for the half load test. Both No. 2 results also indicate an increase in NO_x levels with increasing unit load.

For the overfire air studies, plots of CO emission levels and carbon heat loss versus FA produced the same trend that was established in the baseline operation studies. The CO levels and carbon heat losses were found to increase with decreasing theoretical air in FA.

Boiler Performance

Figure 19 is a plot of unit efficiency versus excess air for the full load tests performed on the subject units. As can be seen in Figure 19, staged firing and overfire air boiler operation did not affect unit efficiency. In a previous section, it was shown that NO_x emission levels can be reduced through the use of overfire air. Therefore, these results indicate that it may be

possible to reduce NO_x emission levels without adversely affecting boiler performance or operation.

In general, unit efficiency is found to decrease with increasing excess air. The decrease in unit efficiency with increasing excess air levels can be attributed to the increasing economizer outlet gas flows and temperatures and therefore to increased dry gas losses.

The two to three percent difference in unit efficiency between Columbia Energy Center, Unit No. 1 and Harry No. 2 or Huntington No. 2 can be attributed to higher dry gas losses and moisture in the fuel losses for Columbia No. 1. These higher losses are due to the type of coal being fired at Columbia No. 1.

WATERWALL CORROSION COUPON EVALUATION

Thirty-day waterwall corrosion coupon evaluations were performed at the baseline and optimum overfire air conditions for each unit. The purpose of these evaluations was to determine what effect low excess air or staged combustion would have on waterwall tube wastage.

The method used to evaluate corrosive potential, waterwall tube wastage, in a boiler is to expose samples of tube material to furnace conditions for finite periods of time and then measuring the weight losses. This is accomplished by inserting test probes each consisting of five coupons into the furnace fuel firing zone and maintaining them at typical waterwall metal temperatures. Figure 20 depicts the type of probe and coupons used to obtain such information. This particular probe utilized air to keep the coupon at the desired temperature.

Typical instrumentation to automatically maintain the desired temperature consists of an electronic controller, and a pneumatic controller. The pneumatic controller operates as a switching device, using solenoid valves, to regulate the amount of cooling air to the probe. The amount of air is based on a signal from the electronic controller, which is tied into the sensing thermocouple at the probe coupon.

At the end of the exposure period, the coupons are evaluated for weight loss and visual evidence of attack. The average weight losses for the baseline and overfire air modes of boiler operation are shown in the following

table. The results indicate that waterwall tube wastage is unaffected by mode of boiler operation.

AVERAGE CORROSION COUPON WEIGHT LOSSES

Unit	Baseline Operation	Overfire Air Operation
Alabama Power Company Barry Station No. 2	2.6181 mg/cm^2	4.4419 mg/cm^2
Wisconsin Power & Light Co. Columbia Energy Center No. 1	8.0770 mg/cm^2	8.0911 mg/cm^2
Utah Power & Light Co. Huntington Station No. 2	1.4266 mg/cm^2	2.6151 mg/cm^2

The weight losses for Barry No. 2 and Huntington No. 2 are within the range of losses that would be expected for the oxidation of carbon steel for a thirty-day period. This premise was verified by control studies conducted in ICF Power Systems' Kreisinger Development Laboratory.

The weight losses measured at Columbia No. 1 are slightly higher than expected. One possible reason for the higher losses is that some of the probes overheated during the thirty-day tests. Another possible reason for the higher weight losses is that the coal being burned at Columbia No. 1 is sub-bituminous, while the Barry and Huntington units both burn bituminous type coals. The results for the Columbia tests, however, show the weight losses are equivalent, regardless of the mode of boiler operation.

SUMMARY

Percent excess air, bulk flame temperature, and residence time of the combustion gases, all directly affect the formation of oxides of nitrogen (NO_x). The two oxides of nitrogen that are significant are nitric oxide (NO) and nitrogen dioxide (NO_2). NO is more predominant and accounts for 90 to 95 percent of the total NO_x generated in a utility boiler. Once it enters the atmosphere, NO is converted to NO_2, which is more hazardous to human health. Most references in this report to NO_2 are actually referring to total nitrogen oxides. This method of expressing NO_x as NO_2 is in agreement with EPA practice.

While it is not the subject of this report, it should be noted that NO_x generated by the combustion of coal can occur by two mechanisms. One mechanism is by the oxidation of atmospheric nitrogen (thermal NO_x); while the other mechanism involves the conversion of fuel-bound nitrogen (fuel NO_x). The formation of thermal NO_x is known to be dependent on flame temperature, oxygen concentration in the combustion zone, and residence time at temperature.

Several investigators have observed that the formation of fuel NO_x is responsible for a significant portion of the total NO_x emitted from the combustion process (1-3). The reaction can take place at a much lower flame temperature and has also been shown to be dependent on the oxygen concentration in the combustion zone. The coals being fired at Barry No. 2 and Huntington Canyon No. 2 had analyses ranging from 1.1 to 1.3 percent nitrogen by weight; Columbia No. 1 had an analysis ranging from 0.6 to 0.8 percent nitrogen by weight. Preliminary plots of NO_2 versus the coal nitrogen content did not show any correlation between NO_2 and coal nitrogen content. Any correlation would probably have been masked by the limited range of the nitrogen content of the coals being fired and by the variation in excess air levels.

The test programs conducted on the subject units showed that overfire air operation is effective in reducing NO_x emission levels. Reductions in NO_x emission levels can be accomplished without adversely affecting unit performance. Mill loading was found to have a minimal effect on NO_x formation, while waterwall slag conditions showed wide and inconsistent effects on NO_x emission levels.

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TABLE I. MAJOR DESIGN FEATURES OF TEST UNITS

	Barry No. 2	Huntington Canyon No. 2	Columbia No. 1
Generator rating, Mw	125	400	520
Main steam flow @ MCR (lb/hr)	900,000	1,036,000	1,800,000
(kg/s)	113	182	479
Reheat steam flow @ MCR (lb/hr)	800,000	2,787,000	3,192,000
(kg/s)	101	351	422
Superheat outlet temp. (F)	1000	1005	1005
(C)	538	541	541
Superheat outlet press. (PSIG)	1875	2645	2620
(MN/m^2)	12.9	18.2	18.1
Reheat outlet temp. (F)	1000	1005	1005
(C)	538	541	541
Reheat outlet press. (PSIG)	404	559	556
(MN/m^2)	2.8	3.8	3.8
Mills (number)	5	6	6
Fuel elevations	4	5	6

TABLE II. AVERAGE PROPERTIES OF COALS TESTED

	Barry No. 2	Huntington Canyon No. 2	Columbia No. 1
Carbon	65.6	66.8	58.8
Hydrogen	4.3	5.1	5.5
Nitrogen	1.4	1.4	0.7
Oxygen	7.6	18.6	12.2
Sulfur	2.3	0.5	0.8
Moisture	8.8	8.0	25.9
High heating value (Btu/lb)	11,701	12,110	8,585

TABLE III. INSTRUMENTS AND ANALYTICAL PROCEDURES FOR MONITORING UNIT PERFORMANCE

	Parameter	Instrument/ Analytical Procedure
Flow rates	Steam and Water	
	Feedwater flow	Flow orifice
	Reheat and superheat desuperheat spray	Heat balance (deg. F & Psia) around desuperheater
	Reheat flow	Heat balance around reheat extraction and estimated turbine gland seal losses
	Air and Gas	
	Total Air and Gas Weight	Calculated
	Inorifice air	Pitot traverse
	Air heater leakage	Paramagnetic O2 analyzer
Temperatures	Steam and Water Deg. F	
	Unit absorption rates	Calibrated stainless sheathed CR-C well & button T/C's
	Waterwall absorption	Calibrated stainless steel sheathed CR-C chromel WW T/C's
	Air and Gas Deg. F	CR-C T/C's Water cooled platen Pt/Pt-10% Rh T/C's
Pressures	Steam and Water Psig	
	Unit absorption rates	Pressure gauges and/or transducers
	Unit draft loss	Water manometers
	Temperature and Pressure	C-E data logger capability: 500 temperatures, 20 pressures
Laboratory analysis	Fuel and Ash	ASTM procedures

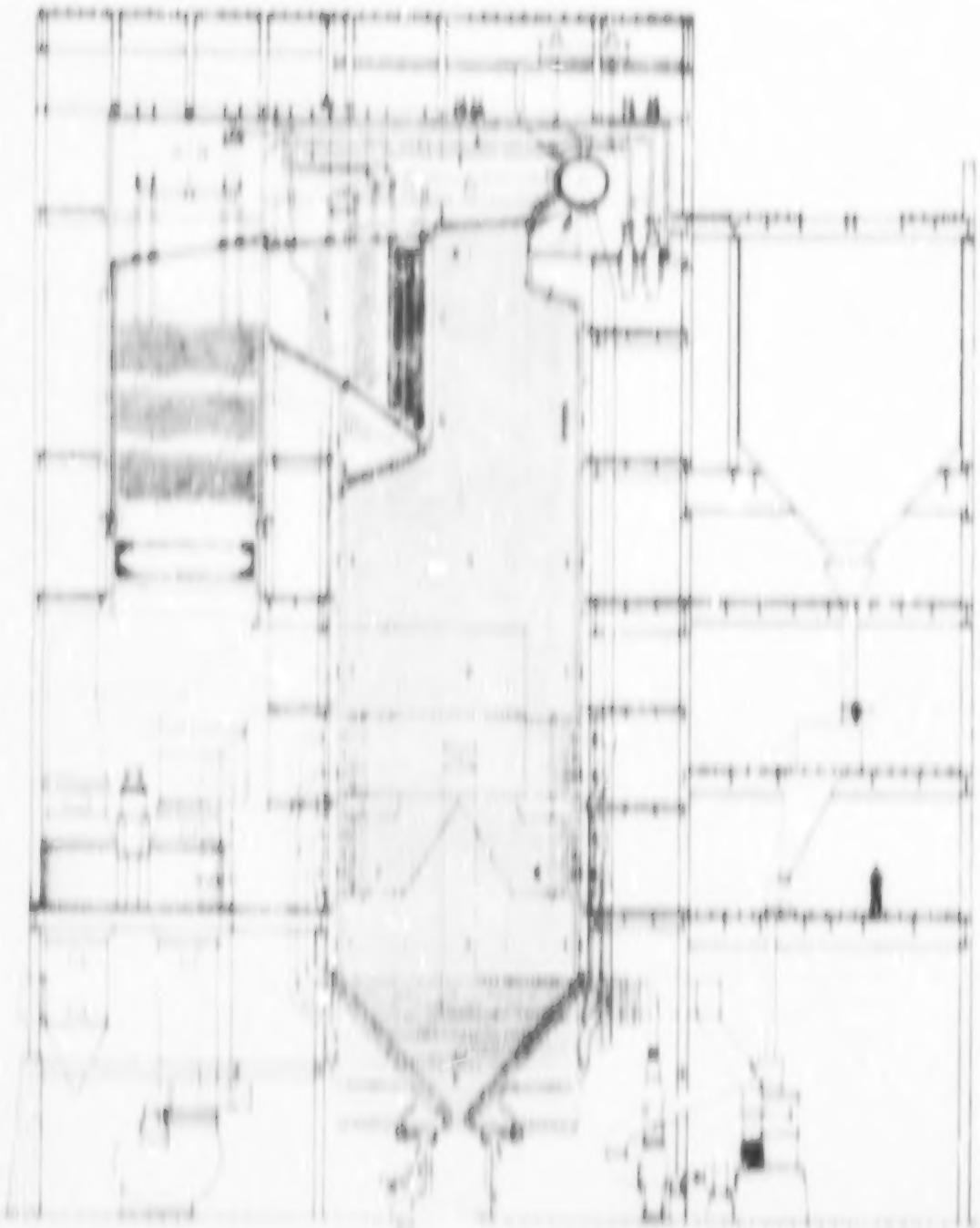
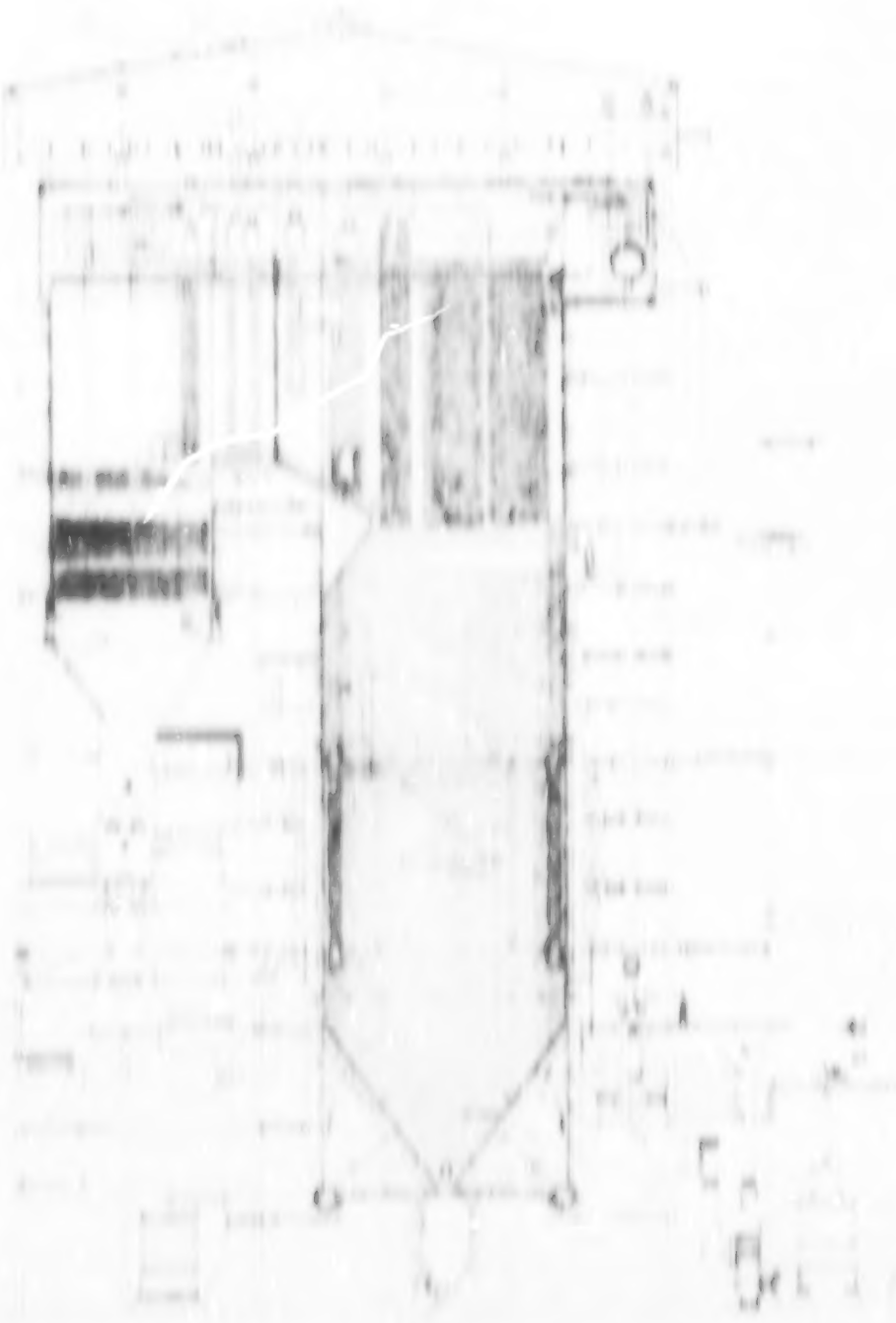


Figure 1. Unit side elevation, Alabama Power Company, Barry Station No. 2



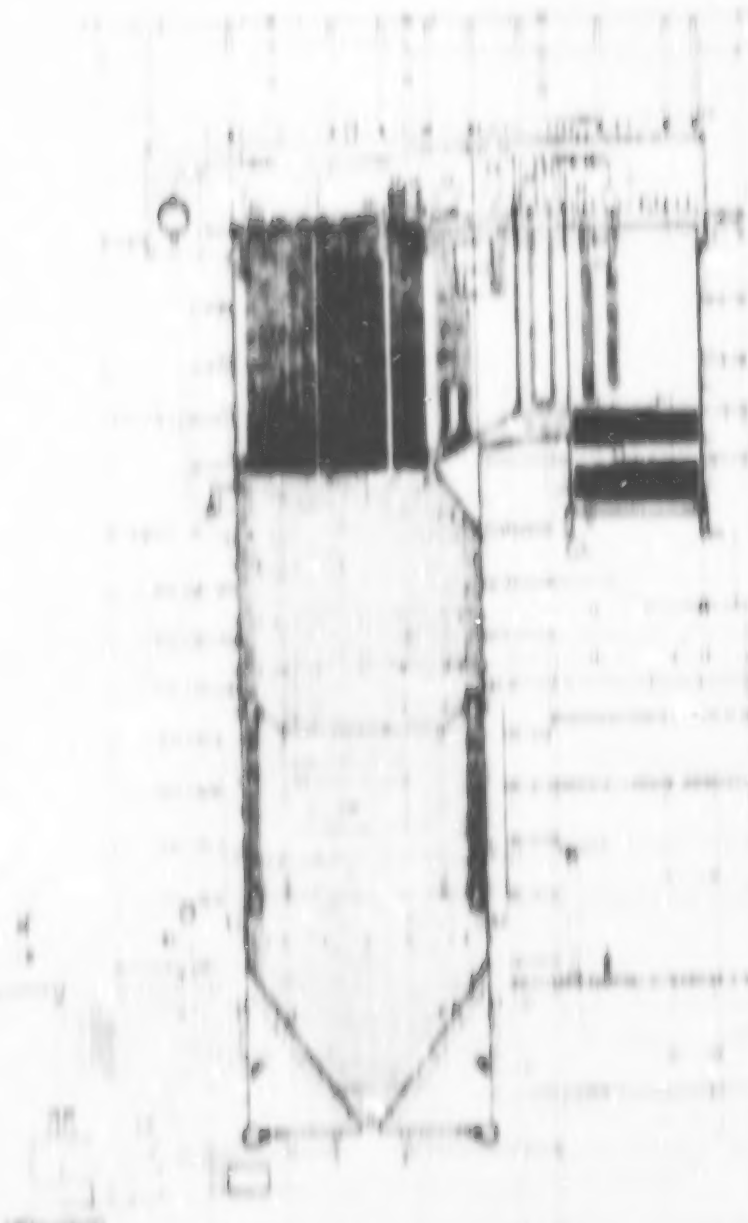


Figure 1. Unit side elevation, Wisconsin Power and Light Company, Columbia Energy Center No. 1

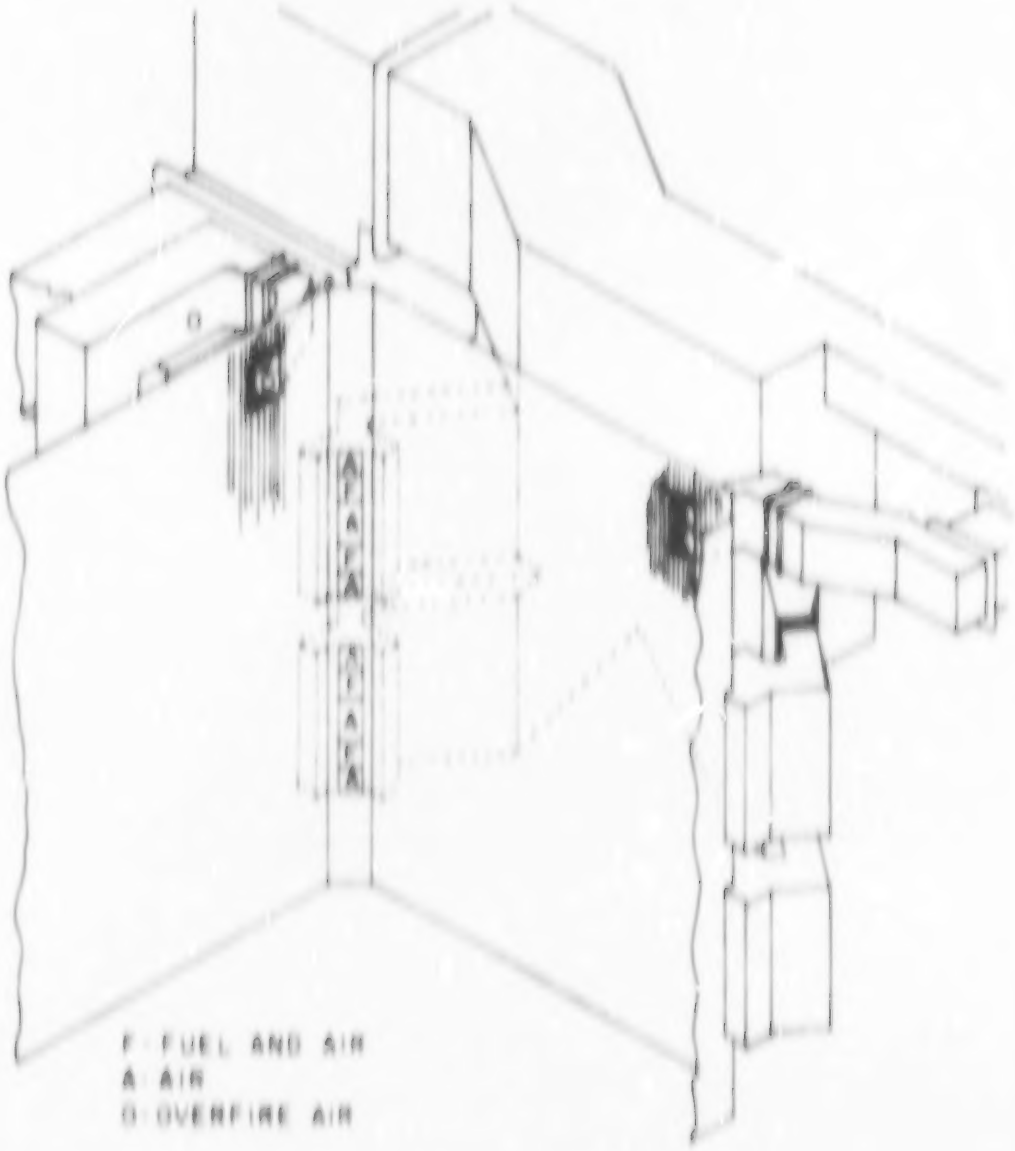


Figure 1. Test unit overfire air system schematic

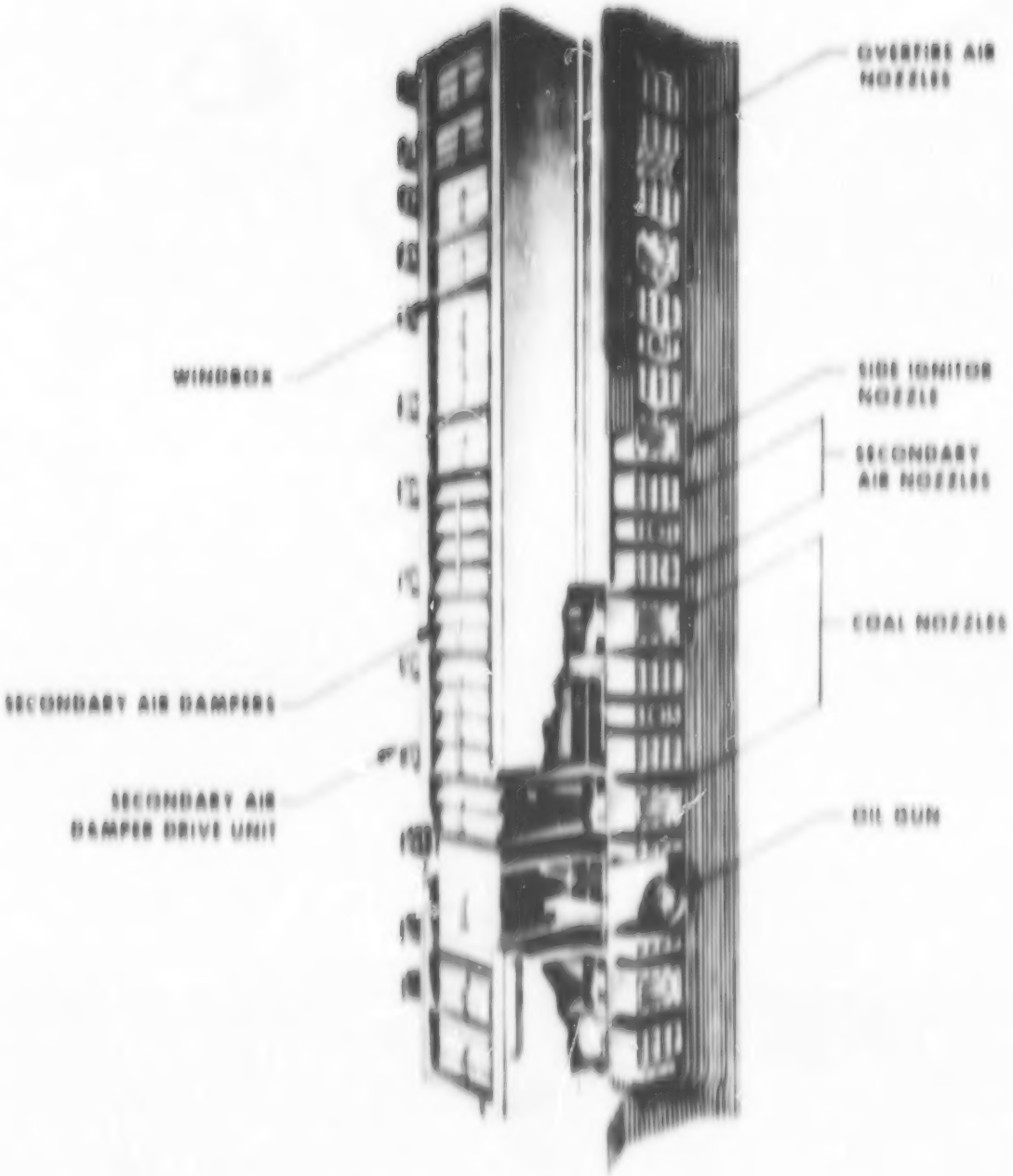


Figure 5. Corner windbox showing overfire air system

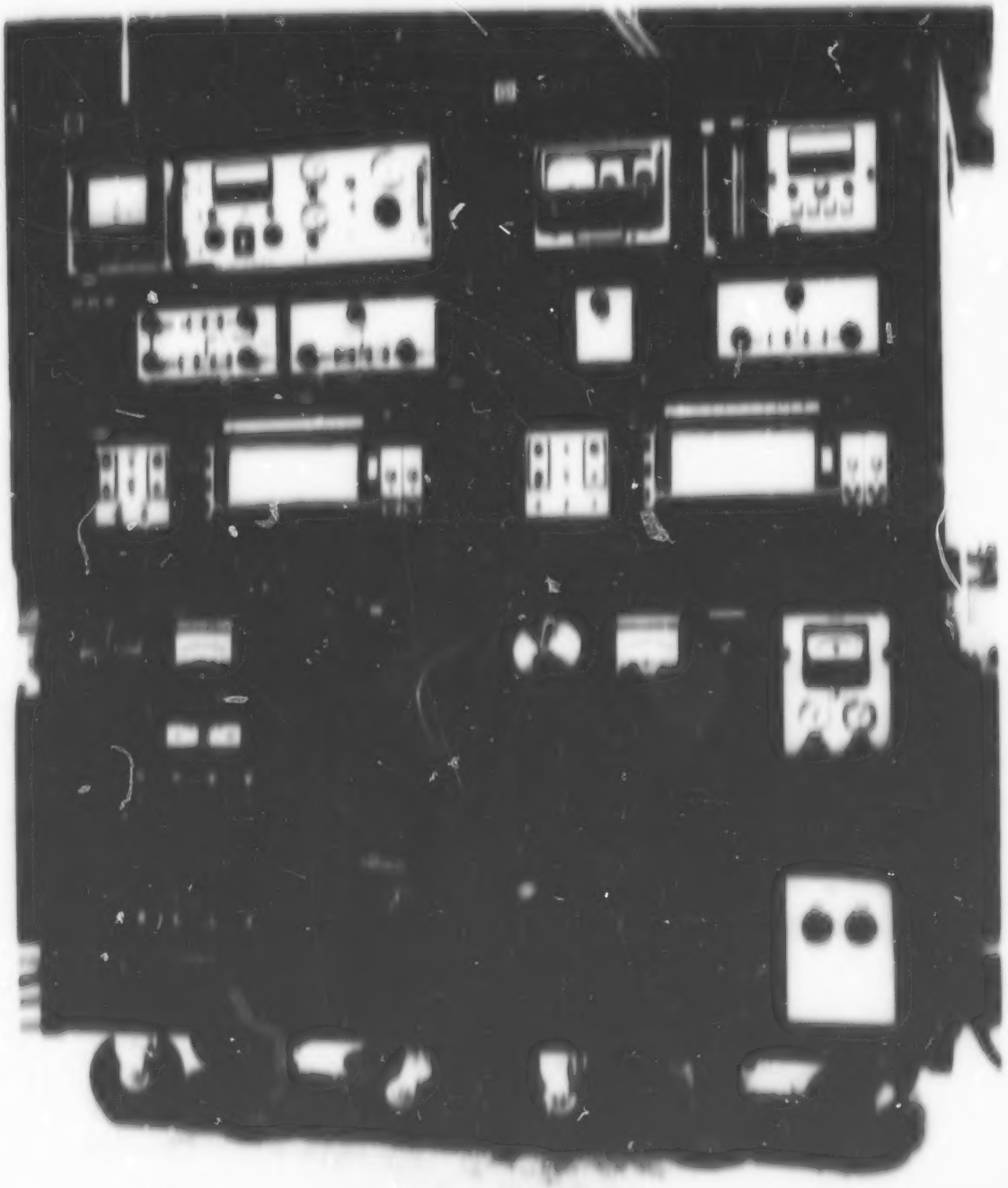


Figure 6: Gaseous emissions test system

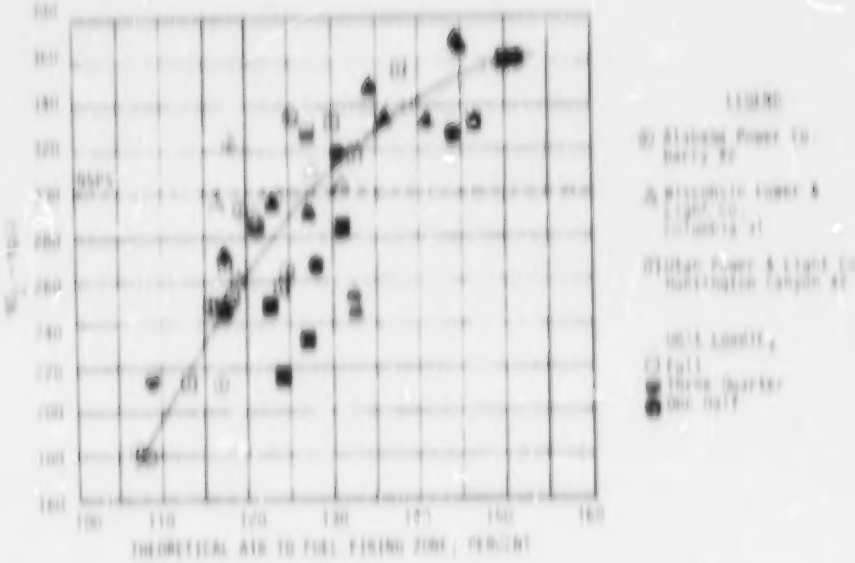


Figure 9. NO_2 vs. unit loading, baseline study

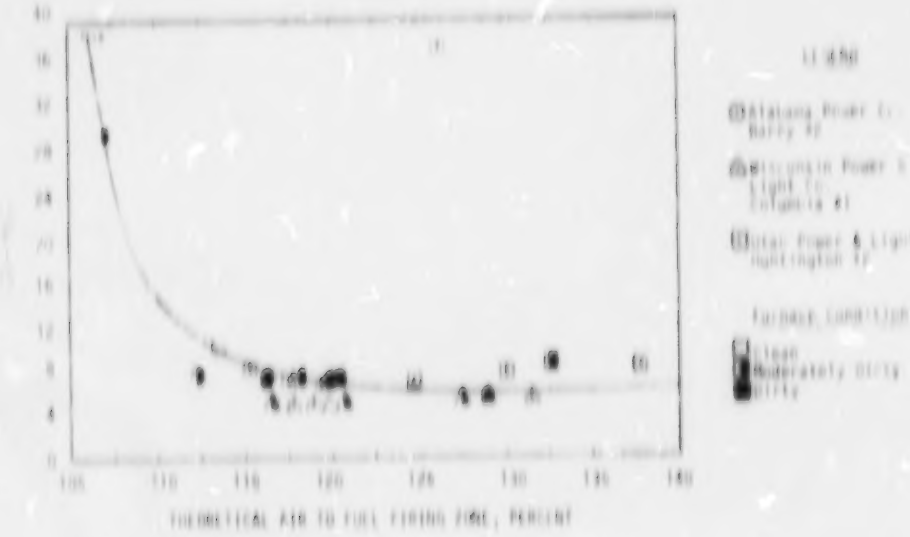


Figure 10. CO vs. theoretical air, baseline study, maximum load

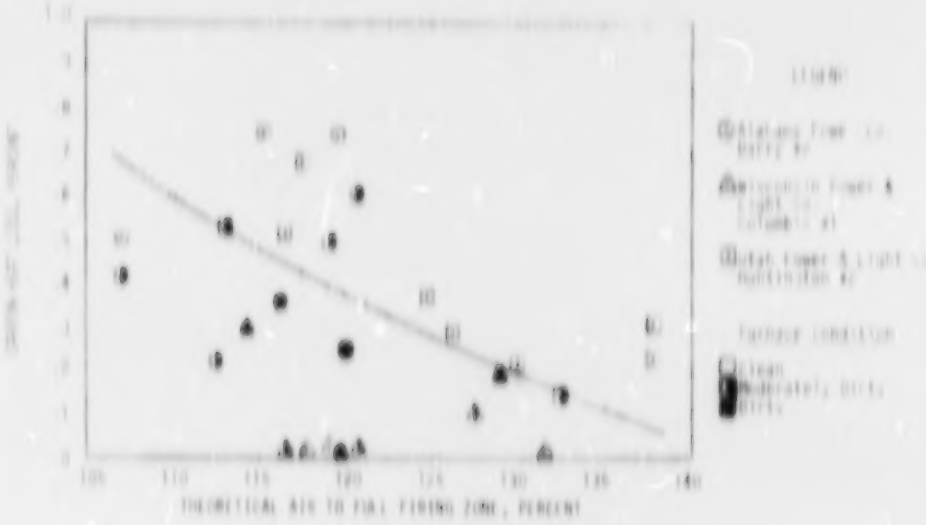


Figure 11. Carbon heat loss vs. theoretical air, baseline study, maximum load

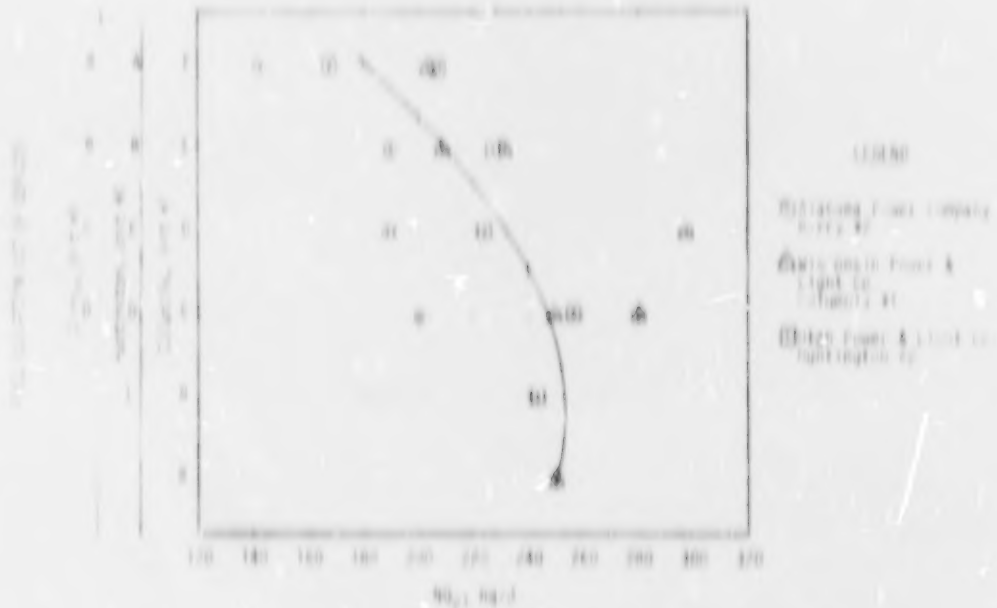


Figure 12. Fuel elevation out of service vs. NO_x, biased firing study

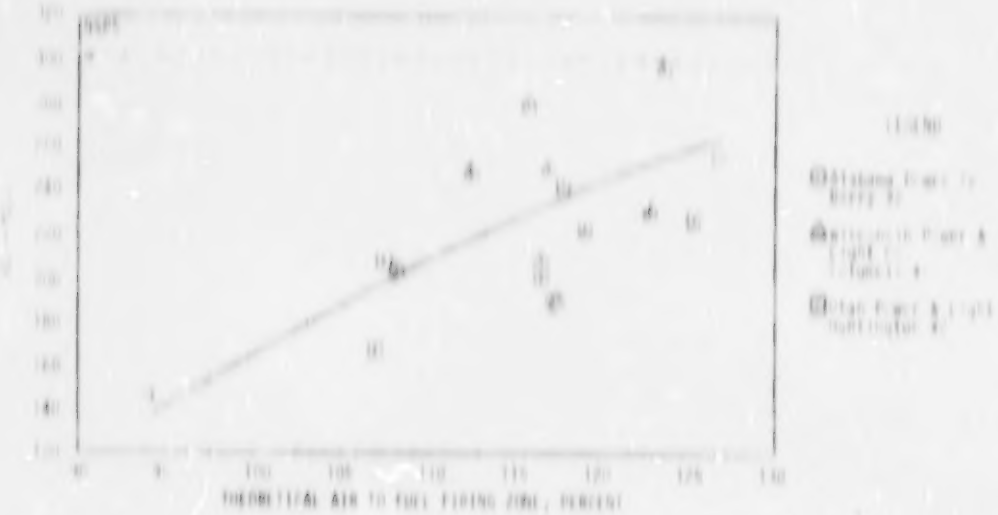


Figure 13. NO_x vs. theoretical air, biased firing study, maximum load

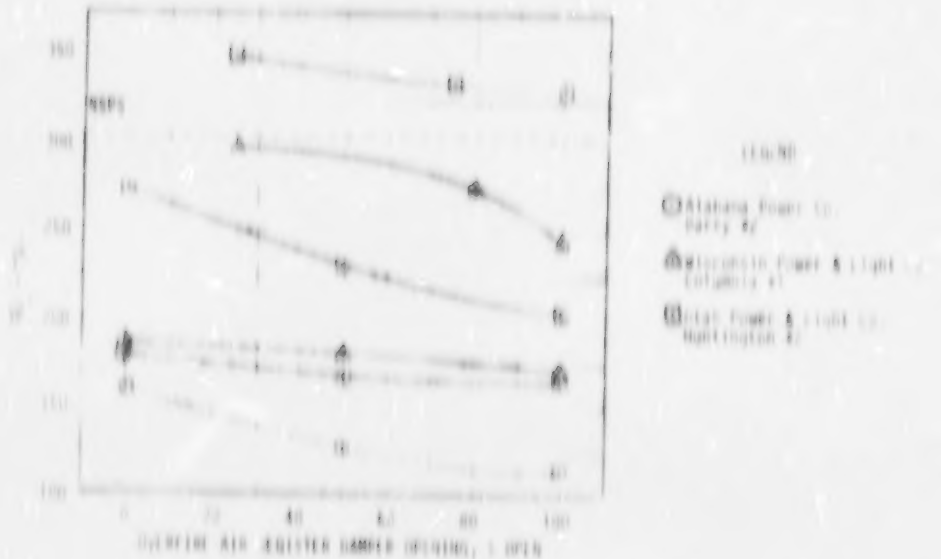


Figure 14. NO_x vs. OFA damper opening, overfire air study

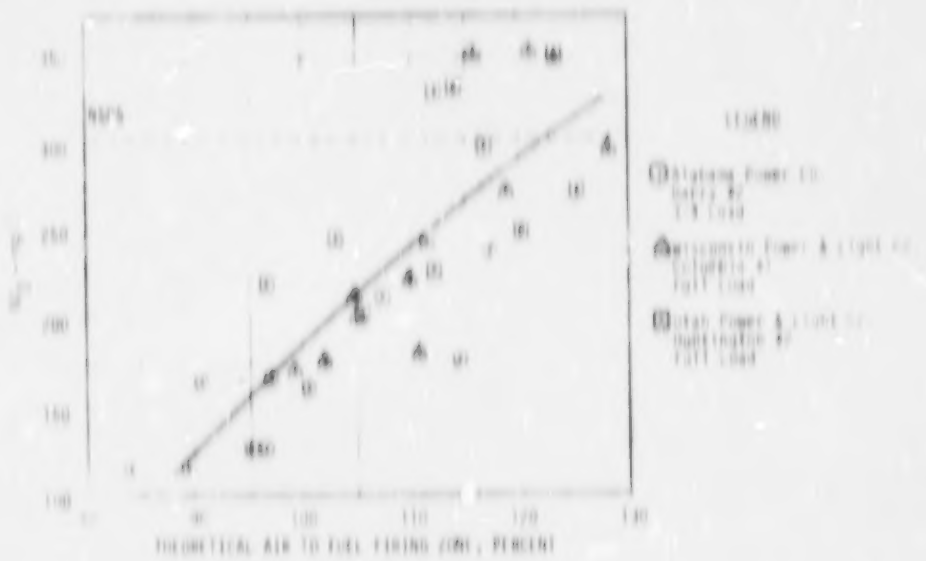


Figure 15. NO_2 vs. theoretical air, overfire air study

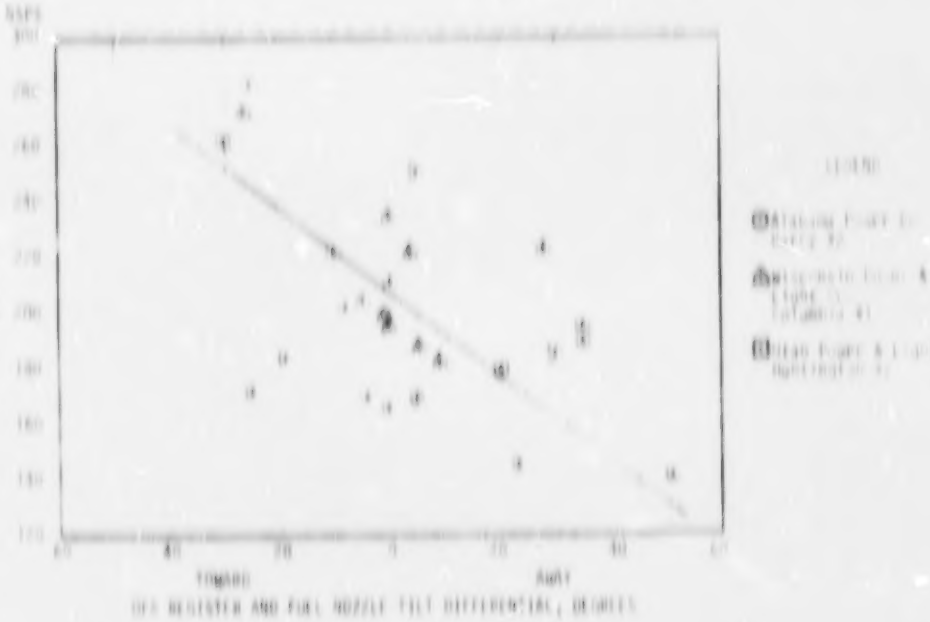


Figure 16. SO_2 vs. tilt differential, overfire air study

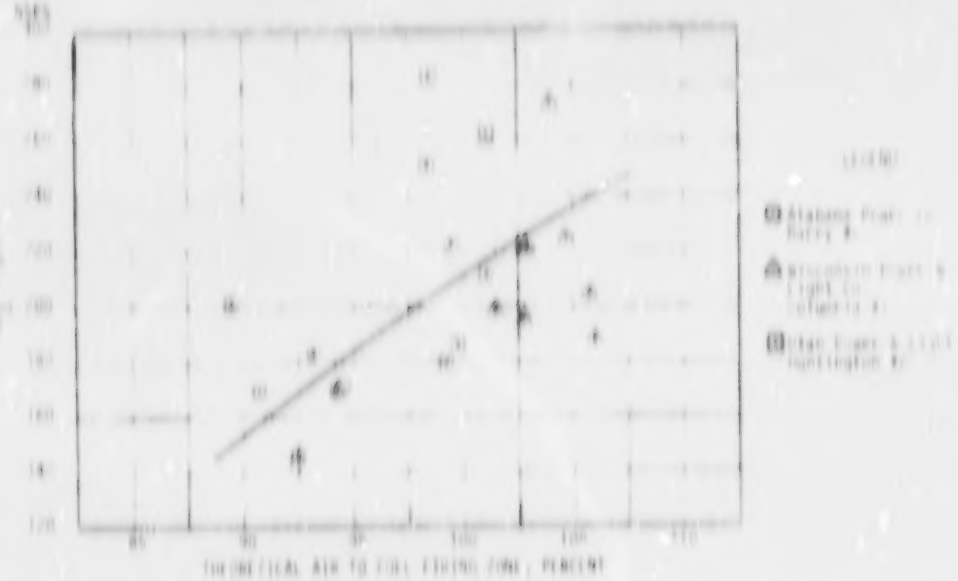


Figure 17. NO_x vs. theoretical air, overfire air study

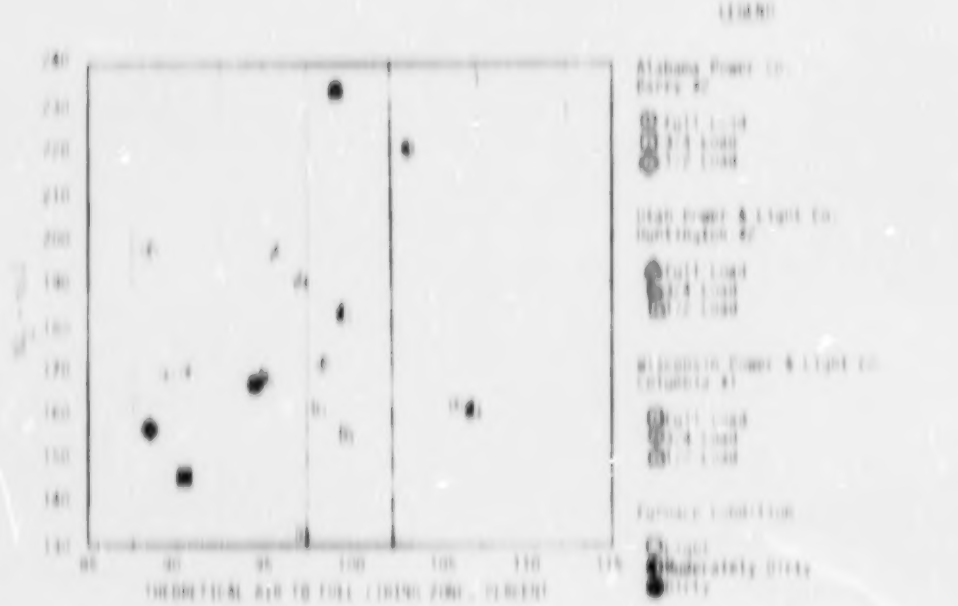


Figure 18. NO_x vs. theoretical air, overfire air study

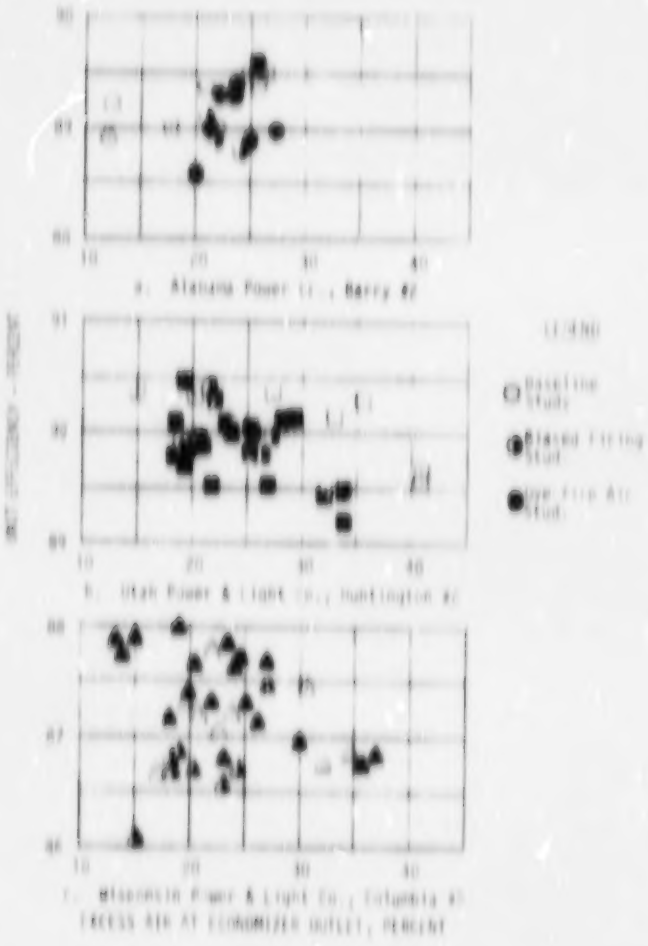

a. Alabama Power Co., Barry #2
b. Utah Power & Light Co., Huntington #2
c. Wisconsin Power & Light Co., Columbia #1
EXCESS AIR AT ECONOMIZER OUTLET, PERCENT

Figure 19. Unit efficiency vs. excess air

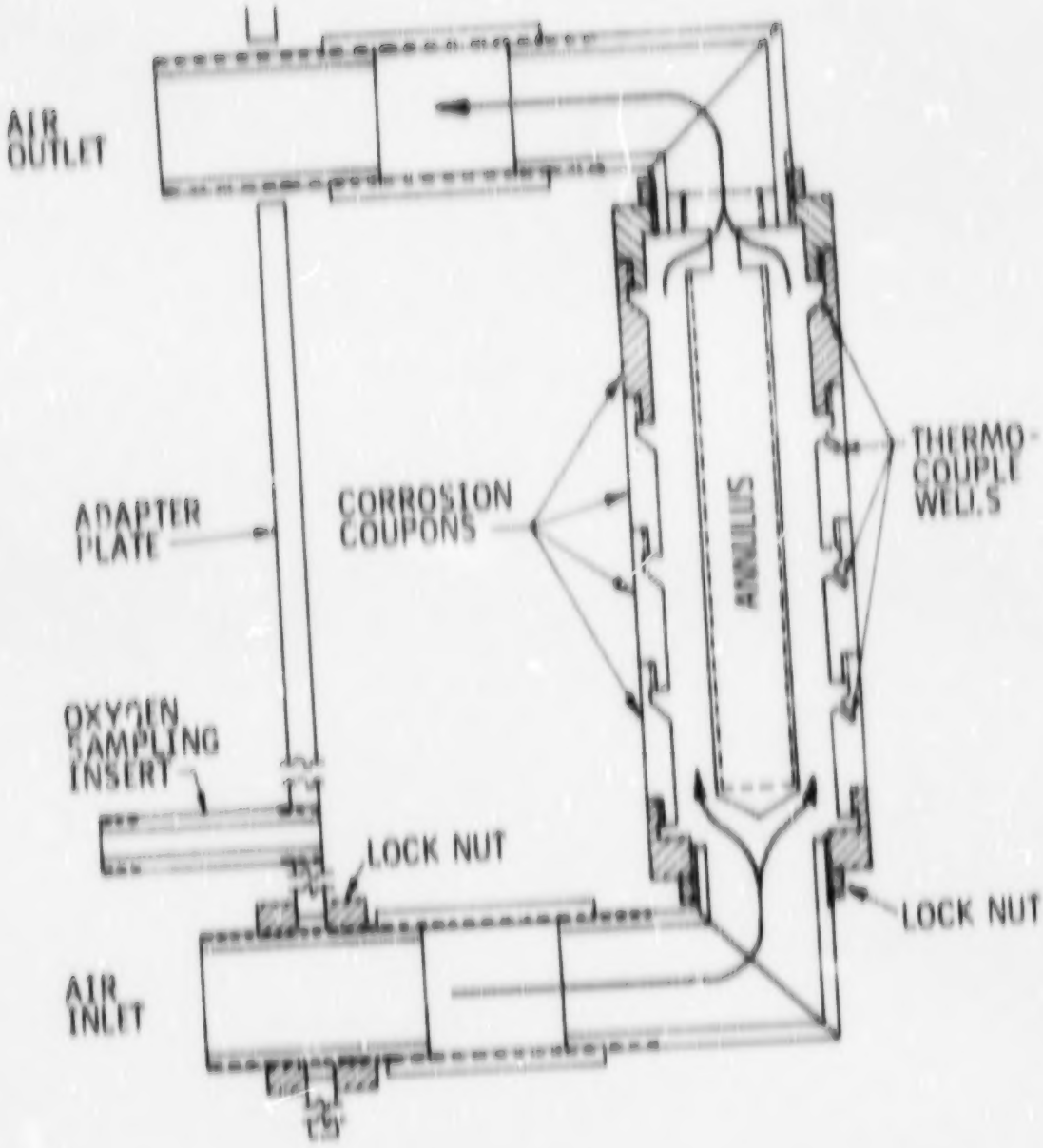


Figure 20. Corrosion probe assembly drawing

THE EPRI PROGRAM ON NO_x CONTROL USING COMBUSTION MODIFICATION TECHNIQUES

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THE EPRI PROGRAM ON NO_x CONTROL USING COMBUSTION MODIFICATION TECHNIQUES

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ABSTRACT

The utility industry, through the Electric Power Research Institute (EPRI), is actively pursuing a significant NO_x control technology program to assure that the NO_x emissions do not become a factor limiting the construction or operation of fossil fueled power plants. The program is directed primarily at understanding the reliability, performance and cost implications of alternative control technologies. This paper specifically reviews the status and results to date from three major combustion control projects in the EPRI program: (1) low-NO_x coal combuction development, (2) selective non-catalytic ammonia reduction of NO_x, (3) low-NO_x turbine combustor development.

The low-NO_x combustion process development is a cofunded project with Babcock & Wilcox. The configuration and design parameters of a two-stage combustion system for coal will be described.

The selective, non-catalytic ammonia reduction of NO_x being performed in cosponsorship with Exxon Research and Engineering Co. is directed at verifying the behavior of ammonia with NO_x in the presence of coal fly ash. The laboratory-scale (3×10^6 Btu/hr) examination of four bituminous and subbituminous coals will be described.

The objective of the low-NO_x turbine combustor development program is to evaluate the potential for a gas turbine combustor capable of meeting 75 ppm NO_x at 15% O_2 without water injection. The performance of dry control configurations incorporating pre-mixing coincidental with prevaporization will be described.

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THE EPRI PROGRAM ON NO_x CONTROL USING COMBUSTION MODIFICATION TECHNIQUES

INTRODUCTION

Of the three major pollutants (SO_x, particulates and NO_x) emitted by power plants, only NO_x is limited to a current control efficiency of 10 to 50%. The utility industry, through the Electric Power Research Institute (EPRI), is therefore actively pursuing a significant NO_x control technology program to assure that NO_x emissions do not become a factor limiting the construction or operation of fossil fueled power plants. The program is directed at understanding the reliability, performance and cost implications of alternative control technologies. The objective is to provide the utility industry an informed basis for not only responding to, but also shaping, the future course of NO_x control requirements.

The EPRI NO_x control program, defined in Figure 1, consists of 15 projects and a six-year budget of $12 million. This program is directed to four objective areas: (1) analysis and control of fuel nitrogen conversion, (2) combustion control for steam generators, (3) combustion control for gas turbine/combined cycle power plants, and (4) post-combustion control of NO_x.

Relatively minor changes in burner designs and boiler operating procedures (i.e., staged combustion and low excess air) have been applied to satisfy the 0.7 $lb/10^6$ Btu NO_x standards for coal-fired steam generators recently proposed by EPA, although questions regarding furnace tube corrosion and potentially toxic byproducts, such as polycyclic organic matter, are as yet unanswered. However, EPA is considering lowering NO_x standards even further: EPA research goals of 200 ppm NO_x in 1980 and 100 ppm in 1985 have been identified for pulverized-coal steam generators. Because of the relative simplicity and economic savings, the emphasis on NO_x control at EPRI has been on combustion modification. A lower priority has been placed on post-combustion alternatives because of the substantially higher costs involved and the likelihood of major reliability impacts.

This paper reviews the status and results to date from three major combustion control projects: (1) the low-NO_x boiler combustion development, (2) selective non-catalytic ammonia reduction of NO_x, and (3) low-NO_x turbine combustor development.

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LOW NO_x BOILER COMBUSTION PROCESS DEVELOPMENT (RP899)

The major problem in trying to achieve low NO_x levels from coal is similar to that encountered with sulfur -- the nitrogen organically bound within the coal molecules is a major source of the emissions. Were this fuel-bound nitrogen not present, such control technologies as wind-box flue gas recirculation and staged combustion would be adequate to control NO_x to very low levels, as evidenced by considerable data from natural gas and residual oil-fired boilers. The fuel-bound nitrogen, however, is unlike its sulfur counterpart in that it does not necessarily result in a solid byproduct scrubber sludge, sulfuric acid, or even elemental sulfur that somehow must be disposed of. There is a considerable amount of data indicating that the fuel nitrogen may be reduced to molecular nitrogen by properly manipulating the combustion chemistry.

The fundamental requirement to accomplish the conversion of fuel nitrogen to N_2 is through fuel-rich combustion. However, this probably cannot be accomplished by an extension of current staged-combustion techniques with conventional burners. More likely, it will require a completely new burner technology that can provide the proper temperature, time and stoichiometry specifically for low NO_x. The system must physically isolate the fuel-rich combustion process from the secondary air injection zone, which is required to maintain an overall oxidizing condition in the boiler. One such approach is the primary combustion furnace concept (Figure 2) proposed by Babcock & Wilcox (B&W) under EPRI project RP899. Pulverized coal is introduced into a conventional B&W dual-register burner with less air than is required for complete combustion. Any resemblance to existing burners ends at this point. The extended length of the combustor provides the necessary residence time to partially oxidize the coal and permit the desirable N_2-producing reactions to occur. Heat removal will also occur along the combustion chamber to avoid slagging. Secondary air is added at the exit of the primary combustion furnace to bring the combustion products to oxidizing conditions for the balance of their passage through a conventional convective section.

The development of the low-NO_x combustion process will be performed on two scales. The first tests will be at 4×10^6 Btu/hr. These tests will evaluate the process variables necessary to accommodate low NO_x while maintaining acceptable combustion characteristics. Heat removal, residence time and quantity of air in the primary combustion furnace are major parameters to be defined. Due to the small scale, only gross aspects of reliability can be evaluated in this research. Following successful completion of testing at the 4×10^6 Btu/hr scale,

research will then move to a 50 x 10^6 Btu/hr facility. This research will confirm the NO_x and combustion process variables determined in the earlier work and evaluate material requirements, mechanical design, and longevity. Results of the 50 x 10^6 Btu/hr tests can be extrapolated to typical full-scale utility burner ratings (150-200 x 10^6 Btu/hr).

Cost estimates for this technology have been provided by B&W. New unit costs are estimated at under $[illegible]/kW and retrofits are projected to be under $20/kW. While these figures must be regarded as preliminary, the attractiveness of the combustion control approach is obvious when one considers that post-combustion control techniques for new units are currently being estimated at $10/kW and up.

Four coal types will be evaluated on this low-NO_x combustor development effort: two Eastern bituminous, one subbituminous and one lignite. Support efforts include: (1) state-of-the-art evaluation of nitrogen conversion chemistry with laboratory study of fuel nitrogen chemistry in both well stirred and plug flow reactors, and (2) analysis of commercial utility steam generator systems incorporating the low-NO_x combustion.

SELECTIVE NON-CATALYTIC NO_x REDUCTION

An alternative to limiting the formation of NO_x through combustion modifications is processes which lead to destruction of combustion-generated NO_x. The gas phase decomposition of nitric oxide is one attractive control approach for NO_x in boiler flue gases. The primary advantage of gas phase decomposition over a catalytic system is the avoidance of the catalyst costs and maintenance problems associated with the more complex catalyst systems. Further, if a selective reduction in nitric oxide occurs, then the amount of reducing agent can be minimized.

The first use of ammonia or reducing NO in a combustion system was reported by Wendt et al. (1). They injected ammonia downstream of the reaction zone of a premixed flat flame operating with 2% excess oxygen. Wendt et al. found that significantly larger reductions in nitric oxide were obtained with ammonia injection than with methane. They attributed this to a pyrolysis of the ammonia to hydrogen in the injector with the hydrogen then reacting with the nitric oxide. Recently, Lyon (2) and Lyon and Longwell (3) have shown that selective gas phase decomposition of nitric oxide can occur in the presence of oxygen by the addition of ammonia to the combustion products. These gas-phase reactions occur over the temperature range of 1200°F to 2000°F. A patent (2) has been issued to Exxon Research and Engineering covering the use of ammonia for the selective homogeneous

reduction of NO_x.

LABORATORY EVALUATION OF THE HOMOGENEOUS GAS-PHASE DECOMPOSITION OF OXIDES OF NITROGEN (RP461)

EPRI, under a contract with RVB, Inc., has experimentally evaluated the potential for selective gas phase NO_x reduction under utility boiler operating conditions (1). The study determined the conditions of reducing agent type, concentration, temperature and time which would lead to the selective reduction of NO_x in the presence of varying amounts of oxygen and nitric oxide. In addition, the study also investigated the potential for NO_x reductions through the injection of reducing agents into fuel-rich combustion products laden with NO_x.

By far the most sensitive parameter in the selective non-catalytic reduction of NO_x is temperature. With ammonia as the reducing agent, a selective homogeneous gas phase reduction of nitric oxide is achieved over the temperature range of 1200°F to 2000°F. This effect of temperature is shown in Figure 2 for typical boiler conditions: an excess oxygen level of 4% and initial NO level of 300 ppm and various amounts of injected ammonia. Significant NO decomposition begins at a temperature of about 1500°F with peak reduction of NO occurring near 1750°F. As the temperature at the point of ammonia injection is further increased above 1750°F, the decomposition of NO by ammonia becomes less effective. At temperatures of about 2000°F, no reduction is observed. In fact, as can be seen in Figure 2, the injected ammonia oxidizes to nitric oxide at temperatures greater than 2100°F. Thus, a temperature window of less than 250°F exists in which substantial reductions in nitric oxide can be achieved with the injection of ammonia into the combustion products.

The ratio of injected ammonia to initial nitric oxide is the second critical parameter in the selective reduction process. As seen in Figure 1, NO reductions vary from 30% to 92% as the ratio of $(NH_3)/(NO)$ varies from 0.1 to 1.6. From the data presented, it may be concluded that a selective reduction in NO is occurring with ammonia injection. For the conditions of Figure 2, a ratio of injected NH_3 to initial NO level of about 106 (based on $NH_3 + 1/4O_2 \rightarrow 1/2N_2 + 3/2H_2O$) would be required to consume all of the excess oxygen and render the combustion products stoichiometric. However, the data show that only trace amounts of ammonia are required, relative to the stoichiometric condition to effect large NO reductions. This is further confirmed since no measureable change in the excess oxygen level occurred over the range of ammonia injection rates studied.

The small-scale laboratory experiments conducted during this study indicated that the selective homogeneous gas phase decomposition of nitric oxide with ammonia or other reducing agents may be a viable emission control technique for conventional utility boilers. Further study is necessary to establish the viability of this approach either as a technique for specialized application, or indeed as a universally applicable approach to NO_x control. Specifically, additional research is needed to confirm the observed NO_x reduction levels on a larger scale. The impact of fly ash and possible reactions between sulfur compounds and the reducing agent on reliability and byproduct emissions also need to be determined. Specific concerns include the potential for NH_4HSO_4 fouling of low temperature heating surfaces and sulfate formation. In addition, evaluation of the feasibility of maintaining the narrow range of effective temperatures necessary for low NO_x emissions in existing and new large utility boilers is required. This information is necessary before determination of the commercial applicability of this technique can be made.

From this study the following specific conclusions may be drawn with regard to the laboratory scale investigation:

1. A selective reduction in nitric oxide occurs when controlled quantities of ammonia are injected into the combustion products.

2. The temperature region in which the selective reduction of NO_x occurs is between approximately $1300^{\circ}F$ and $2000^{\circ}F$, with the peak reductions taking place at about $1750^{\circ}F$ with ammonia injection.

3. At the peak reduction temperature, a ratio of injected ammonia to initial NO of unity yielded an 80% reduction.

4. The NO is primarily reduced to molecular nitrogen (N_2).

5. Ammonia emissions were maintained at less than 10 ppm if the reducing agent is injected at a temperature slightly higher than the peak effectiveness temperature. This results in the excess reducing agent being consumed by the excess oxygen.

6. The tests further indicate that the presence of sulfur oxides in the combustion products had no measurable effect on the NO reductions obtained.

7. Selective removal of NO can also be achieved by the injection of other amine species (e.g., CH_3NH_2, $(CH_3)_2NH$, and $(CH_3)_3N$); however, these are of little practical interest.

8. When ethane, methane, carbon monoxide, or hydrogen are used as reducing agents, a nonselective reduction occurs with significant nitric oxide reductions occurring only when the combustion products become fuel rich.

9. Ammonia, ethane, and methane were also effective in reducing nitric oxide in fuel rich combustion products. For this case, the maximum reductions occur at higher temperatures (typically greater than 2100°F) with ammonia again being the most effective reducing agent.

LABORATORY EVALUATION OF COAL-FIRED NO_x REDUCTION WITH AMMONIA REJECTION (RP834)

Under project RP834, EPRI is continuing to investigate the direct reduction of NO_x with ammonia rejection, specifically as it applies to coal combustion. This effort is being conducted in cosponsorship with Exxon Research and Engineering Company at KVB, Inc. The research is directed at determining the levels of NO_x removal possible for four different coals (New Mexico subbituminous, Pittsburgh Seam 8 bituminous, Illinois No. 6 bituminous and Utah low-sulfur bituminous) using selective, noncatalytic ammonia injection. Tests are also being performed to (1) obtain data on the type and concentration of potential byproduct emissions, and (2) determine the extent to which hydrogen can lower the effective process temperature range.

The tests will be conducted in the KVB 1 x 10^6 Btu/hr facility. A test matrix, as shown in Figure 4, will be undertaken to determine the effect of temperature, ammonia injection rate and coal type.

EVALUATION OF A PREMIXED, PREVAPORIZED GAS TURBINE COMBUSTOR (RP159)

In addition to the regulations being considered for pulverized-coal power plants, EPA has issued proposed emissions standards for industrial gas turbines. NO_x emissions will be limited to 75 ppm at 15% O_2 for both liquid and gaseous fuels.

The only means currently available for meeting these standards involve water (or steam) injection into the combustor. Unfortunately, this technique has a capital cost of at least $10-$15/kW and a fuel consumption increase of 2-3%. Increased maintenance costs are also probable, so a system that avoids water injection is desirable. In conjunction with Solar Division, International Harvester Company, EPRI has undertaken a project to evaluate the feasibility of a low-emission combustor that does not use water or steam. This is commonly referred to as the dry approach.

There are several ways of controlling NO_x without water injection. All these, however, require that the fuel and air be completely mixed prior to combustion. The most difficult conventional fuel to accommodate is No. 2 distillate because it must be vaporized as well as mixed before combustion occurs. Accordingly, most research has centered on this fuel. The most common premixed combustion method uses high-pressure (10 atm) and high-temperature (650°F) combustor inlet air to provide the heat of vaporization of the distillate oil. Figure 5 is a diagram of the combustor tested. The main fuel injection is into the premixing ports. During its passage through the ports, the fuel is evaporated and mixed to a uniform stoichiometry with the airstream. At this point, the fuel-air charge enters the primary zone, where combustion occurs. Subsequent secondary and dilution zones are designed to use essentially conventional combustor design principles. Fuel can also be introduced through the pre-combustor. This provides the capability to independently vary inlet air temperature and also permits added turndown flexibility.

Preliminary results of the emissions performance of the dry combustor have been obtained (5). Up to about 7 atm combustor pressure, emissions are within proposed EPA standards. However, at the design operating pressure of 10 atm, emissions several times higher than required were observed. The probable cause of the high emissions is incomplete evaporation and mixing of the fuel in the vaporization tubes. One solution to improved fuel vaporization is increased combustor inlet air temperatures. However, increasing the temperature produced autoignition of the fuel-air mixture in the vaporization tubes. Autoignition resulted in failure of the fuel preparation ports.

The autoignition results can also be interpreted in terms of mixing rates. Slow mixing between vaporizing fuel and air favor locally high equivalence ratios. These higher-than-average ratios can then produce autoignition at conditions other than those governed by chemical processes at the overall stoichiometry. These considerations form the basis for future tests involving the effect of increased initial fuel dispersion (more fuel injection sites) and droplet size.

Although the evaporation/autoignition problem may be resolved through one or more of the techniques described, the solution may still be of only academic interest if practical problems of safety, reliability and availability are considered. For example, a perfectly acceptable solution to autoignition may be to use a fuel injector with more than four fuel injection sites and larger vaporizing ports at compressor exit air temperature entering the vaporization tubes. However, the system may be

marginally stable, and only a minor perturbation in flow or temperature could lead to catastrophic results.

Other problem situations are conceivable. For example, if 10-point fuel injectors were found to be an acceptable solution, this would mean, for example, in a typical gas turbine having eight cans, with six premixing tubes per can and each premixer tube having the requisite 10-point fuel injection sites, that 480 fuel injectors would be required. The reliability problems associated with this complexity are clearly high. Finally, if significant blockage of some of the fuel lines were to occur, the balance between a stable vaporization/preignition situation would be disrupted. This could shift the vaporizing/premixing post-equivalence ratio to a value in the autoignition range, with subsequent mechanical failure of the combustor.

Optimistically, a combustor design solution avoiding these potential problems can be developed. It is also clear, however, that this achievement of a dry control method for gas turbine NO_x will require considerable additional research before a commercially acceptable solution can be found.

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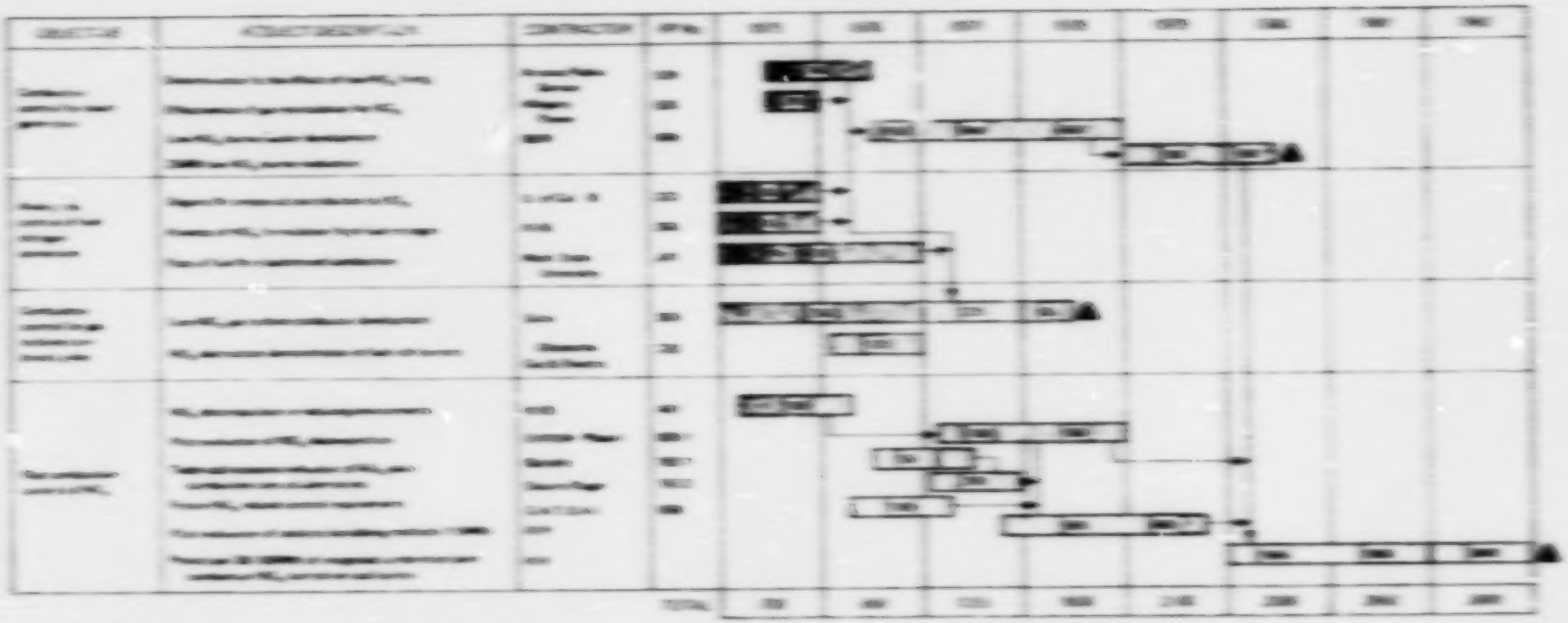
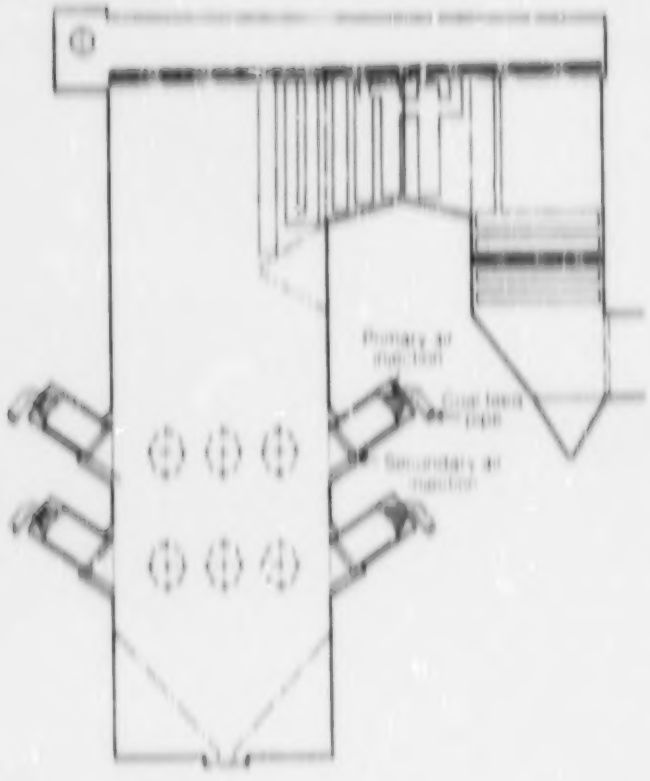


Figure 1.

Figure 2 Primary combustion furnace concept as proposed by Babcock & Wilcox Co. To extended combustion permits N_2 producing reactions to occur



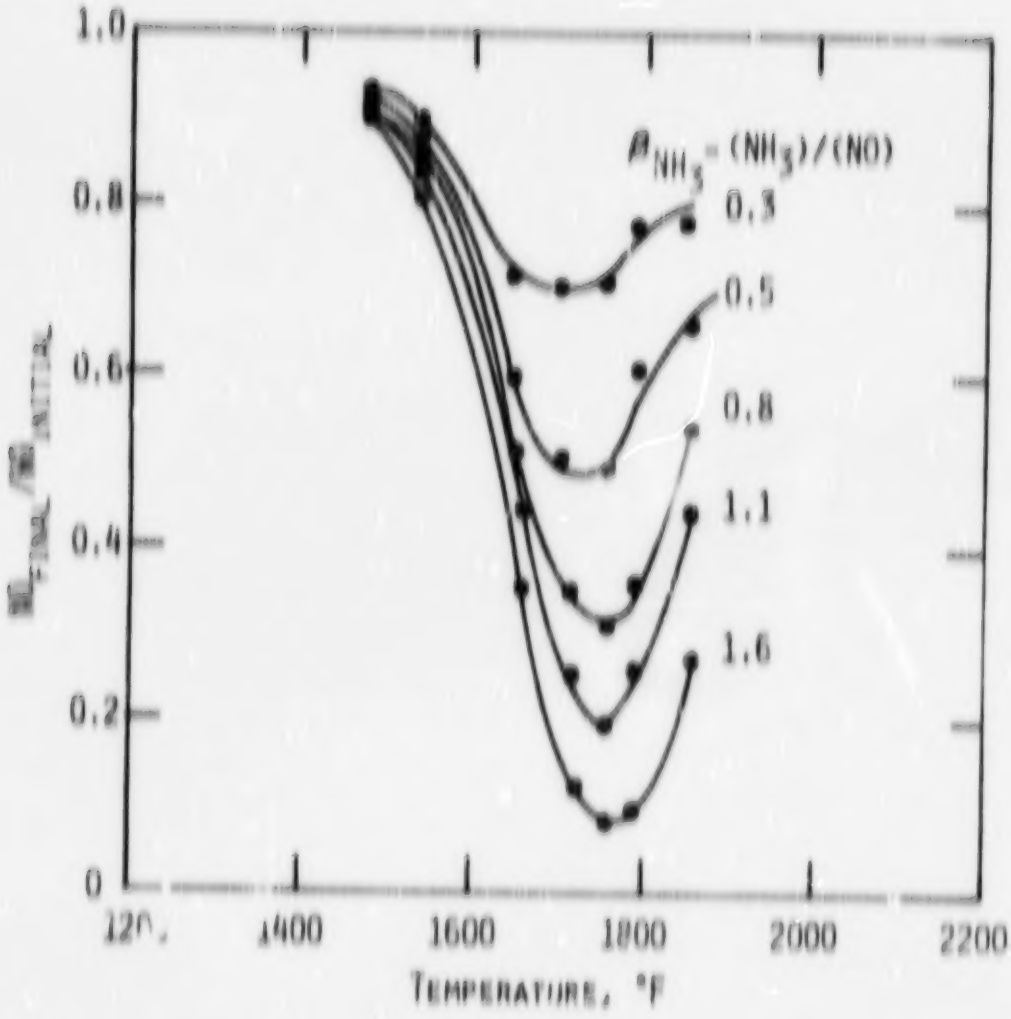


Figure 3. Effect of Temperature on NO Reductions with Ammonia Injection. (Excess Oxygen 4%, Initial NO 300 ppm).

FIGURE 4.

EXPERIMENTAL MATRIX

NH_3 Injection Tests

		Natural Gas	Coal A[b]	Coal B[b]	Coal C[b]	Coal D[b]
Excess Oxygen	Approx. 6%	1	1	1	1	1
NO_x Level	Burner Produced 400-700 ppm	1[c]	1	1	1	1
Temperature at Injection Point	1400°F to 1900°F	4	4	4	4	4
NH_3 Flow Rate[d]	$(NH_3)/(NO)$ = 0-5 molar	4	4	2	2	2
Number of tests with each fuel		16	16	8	8	8

Total NH_3 tests: 56

(a) Numbers indicate the number of variations.
(b) Coal A = New Mexico sub-bituminous;
Coal B = Pittsburgh Seam 8 bituminious;
Coal C = Illinois bituminous;
Coal D = Colorado bituminous;
(c) NO_x will be added to the burner air.
(d) Where there are two NH_3 runs, the ratios will be 1.5:1 and 2.5:1.

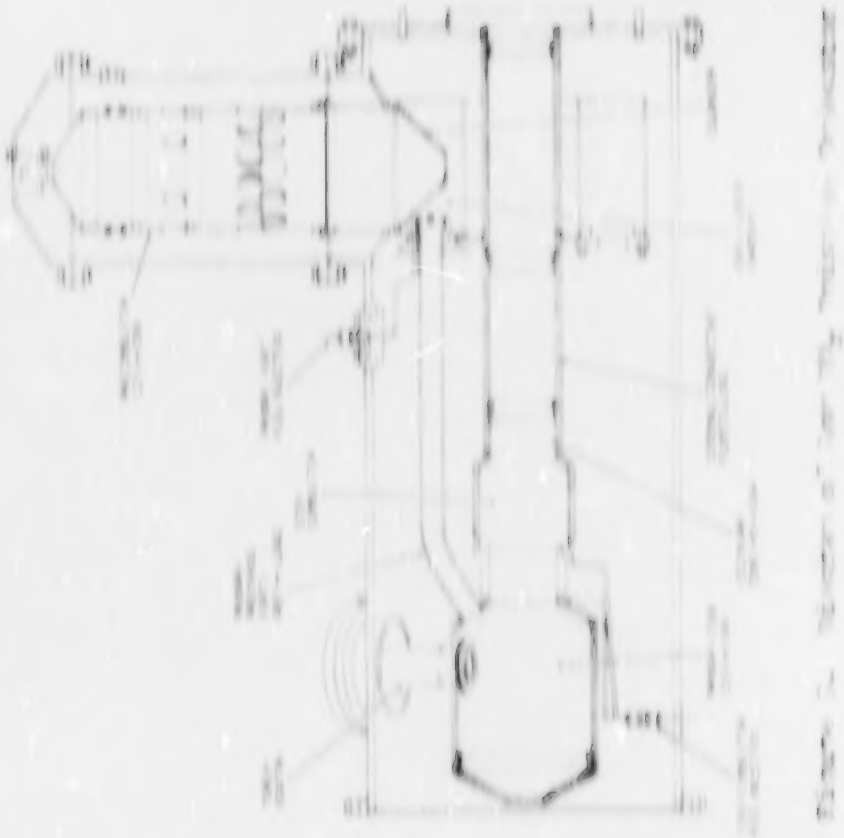
NH_3 + H_2 Injection Tests

Variable	Range	Fuel Type Coal A
Excess Oxygen	Approx. 6%	1
NO_x Level	Burner Produced 400-700 ppm	1
Temperature at Injection Point	1000°F to 1500°F	2
NH_3 Flow Rate	$(NH_3)/(NO)$ = 0-1	2
NH_3 Flow Rate	$(NH_3)/(NO)$ = 0-to be determined	4

Total NH_3 + H_2 Tests: 16

SUMMARY:

Total number of Gas Tests:	16
Total Number of Coal Tests:	56
Total Number of Tests:	72



DESIGN AND SCALE-UP OF LOW EMISSION BURNERS FOR INDUSTRIAL AND UTILITY BOILERS

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This paper was not received in time for publication, and therefore will be included in Volume V.

CYCLONE BOILERS -- THEIR NO_x EMISSIONS AND POPULATION

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ABSTRACT

There are 169 boiler units in the United States that are fired by a total of 736 cyclone furnaces. All of the cyclone furnaces are located in the East and Midwest. Three states, Illinois, Missouri, and Indiana, account for nearly half of the total-fired steaming capacity and one-third of the boilers.

Since cyclonic combustion takes place at high combustion temperatures, cyclone furnaces firing utility and industrial boilers are high NO_x emitters. Based on available data, their measured full-load emissions were 576 ng/J to 716 ng/J for bituminous coal firing, 546 ng/J for subbituminous coal firing, 291 ng/J to 359 ng/J for lignite firing, 217 ng/J to 318 ng/J for residual oil firing, and 208 ng/J to 325 ng/J for natural gas firing.

The authors estimate that 0.76×10^6 metric tons of NO_x were emitted from all cyclone coal-fired utility boilers in 1973. This represents from 19% to 22% of the NO_x produced by all coal-fired utility boilers in the U.S. Correspondingly, between 10% and 13% of coal consumed by all coal-fired utilities was used by cyclone fired units. Similar estimates for industrial boilers could not be obtained due to insufficient data.

Several combustion modification techniques have been applied to cyclone boilers/furnaces in an attempt to lower their NO_x emissions. These include boiler load reduction, low excess air firing, two-stage firing, and switching fuels. Even though significant reductions in NO_x were achieved, none of the techniques was shown to reduce NO_x emissions to the level meeting the EPA's New Source Performance Standards for NO_x.

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ACKNOWLEDGMENT

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SECTION 1

INTRODUCTION

The first cyclone-fired boiler began operation 33 years ago. At that time, cyclone firing represented a major breakthrough in the art of firing troublesome coals high in ash content and having a low ash fusion temperature. Both of these factors, frequently an annoyance to both boiler operators and designers, were an advantage in cyclone furnace operation.

Successful operation of the cyclone furnace depends on maintaining a liquid or wet slag within the cylindrical furnace. Crushed coal (95% will pass through a 4-mesh screen) is introduced tangentially through a primary burner at the front of the cyclone furnace, thrown to the walls of the cyclone, and caught in the running slag, Figure 1. Tangentially supplied secondary air at velocities of 91.4 m/s sweeps past the embedded coal particles, quickly oxidizing them. The cyclone is typically 1.8 m to 3.0 m in diameter and about 1.4 m long and is water-cooled. In order to maintain proper slagging, low furnace heat absorption rates and low ash fusion temperatures are maintained and the cyclone is operated at temperatures as high as 1930 K. Large quantities of fuel are combusted within a relatively small volume, resulting in furnace high heat release rates (5.7 MW/m^3 to 7.8 MW/m^3; a pulverized-coal-fired unit typically has a heat release rate of 0.2 MW/m^3).

Since cyclonic combustion intrinsically requires high combustion temperatures, the cyclone-fired boilers are high NO_x emitters. This paper briefly summarizes information that was compiled on cyclone boiler population and NO_x emissions, both with and without modifications made to decrease such emissions.

SECTION 2

POPULATION

The first full-scale cyclone-furnace-fired boiler was placed on stream in 1946 at the Calumet Station of the Commonwealth Edison Company, Calumet, Illinois. Since then, a total of 84 cyclone-fired installations have been built in the U.S. These installations are located in 26 states, contain a total of 159 boiler units fired by a total of 736 cyclone furnaces, and have a primary steam-generating capability of approximately 26,000 kg/s (about 9% of the total U.S. steam-generating capacity). Illinois, Missouri, and Indiana account for nearly half of the total cyclone steaming capacity and one-third of the boilers. Table 1 gives a further breakdown of the cyclone-fired boiler population. It shows that over 94% of the total primary steaming capacity is held by the electric utility sector (24,253 kg/s) which operates 116 of the 159 boilers. These boilers are fired by 677 furnaces. The remaining 33 boiler units are owned by private industry and institutions. Table 1 also indicates that primary steam-generating capacities of individual boiler units built range from 10 kg/s to 70 kg/s for industrial and commercial units and from 23 kg/s to 1,160 kg/s for the electric utility units. All these units were built by the auto manufacturer or cyclone furnace boilers, Babcock & Wilcox Company, who estimates that the majority of the boilers listed in Table 1 are still in use even though some may have been derated because of their age.

Since about 1973, the Babcock & Wilcox Company has not sold a single cyclone unit. The decline of sales started with the strict Federal SO_2 regulations imposed on new stationary combustion sources. The low ash fusion temperature coals burned in the cyclone boiler normally have a high sulfur content. Switching to low-sulfur coals normally results in ash with a high fusion

temperatures. The final event which restricted the sale of bituminous-coal-fired cyclones was the limitation of NO_x emissions for stationary combustion sources.

SECTION 3

BASELINE EMISSIONS FROM CYCLONE FURNACE INSTALLATIONS

Although all existing cyclone furnaces were originally designed to burn coal, [illegible] other types of fuels have been and are still being successfully fired in them. These fuels include residual and distillate oils, solid wastes (wood bark, coke), and natural gas. Baseline emissions from these units are defined to be those NO_x emissions reflecting normal or near normal boiler operation at various loads. Full-load (91% to 100%) baseline emissions are summarized in Table 11 by type of fuel along with the New Source Performance Standards (NSPS) for NO_x. Data in Table 11 were obtained from 14 boiler units field tested by the Exxon Corporation, the Tennessee Valley Authority, the Babcock & Wilcox Company, KVB, Inc, and NAPCA (EPA).

SECTION 4

CYCLONE COMBUSTION MODIFICATIONS

Only a relatively small number of cyclone boilers were found to have been examined and tested in some way to determine the effects of combustion modifications on NO_x emissions. One reason for the lack of field data on this combustion equipment class is the relative inflexibility of the cyclone furnaces and boilers in respect to combustion process modification. Altering the cyclone operation sufficiently to control NO_x can result in a furnace that is no longer a cyclone.

Four types of combustion modifications have been applied, however, either singly or in combination to reduce NO_x emissions from cyclone furnaces. These are: low excess air firing, load reduction, staging, and switched fuel firing.

Twelve boilers were tested under modified combustion conditions. The modification techniques applied most often have been load reduction and low excess air firing because they require no physical modification or changes of existing cyclone units.

LOW EXCESS AIR FIRING:

In one test performed on a lignite-fired boiler at full load, reduction in the oxygen content of the flue gas by 75% (from 6.4% O_2 to 1.6% O_2) reduced NO_x emissions by 47%. However, CO concentrations increased from 0 vppm to 17 vppm (see Table III). Firing the cyclone with 1.6% O_2 in the flue gas required supplemental oil fuel to maintain ignition.

Likewise, for oil-fired boilers at full load decreasing the excess oxygen lowered NO_x emissions. These results are summarized in Table IV. In no case were NO_x emissions reduced enough to meet the NSPS. The lower NO_x levels achieved by reducing excess air again could not be justified because of the increased levels of CO.

LOAD REDUCTION

Load reduction in cyclone-fired boilers results in consistently lower NO_x emissions compared to the same boilers at full or normal loads. This is usually considered an economically unattractive method for reducing NO_x emissions, however, because of the penalties incurred and because of reduced thermal efficiency and reduced boiler flexibility at reduced loads. Maximum loads reduction for a cyclone boiler appears to be limited to about 40% of the maximum continuous steam rating. Below this point load reduction causes flame instability with possible loss of ignition, lack of adequate steam temperature control, and excessive slagging on the cyclone walls when coal is fired. Five of six units tested showed an overall reduction of NO_x emissions as load was reduced. Two of these boilers were oil-fired. With minor extrapolation it was possible to compare the results from the five boilers, as shown in Figure 7.

With a 20% reduction in load, three bituminous-coal-fired units showed a reduction in NO_x emissions ranging between 24% and 12%. For the same load reduction two oil-fired boilers showed NO_x emission reductions ranging between 8% and 10%. With the exception of one oil-fired boiler operating at the reduced load of 57%, the reduction in NO_x emissions was nevertheless inadequate to meet NSPS.

STAGING

Staging requires physical modification of the cyclone boiler. There are definite limits to the extent to which existing units can be modified, however. Consequently, the field test data obtained under staged firing conditions are

limited in nature and representative only of the specific conditions and arrangements existing during the tests.

Staged firing is based on sustaining the initial part of the combustion in a reducing atmosphere zone. Several forms of staged firing have been applied to cyclone boilers, mainly two-staging and pattern firing.

Applying two-staging to the cyclone boiler involves reduction of the amount of combustion air fed into the cyclone. The remainder of the air is sent into the boiler at a point near the exit of the cyclone furnace proper.

Two-staging has been applied to an eastern-coal-fired boiler and a gas-fired boiler. The first unit showed a 28% to 36% reduction in NO_x emissions. However, when firing coal, two-staging may require an oil supplement to maintain ignition and flame stability. The gas-fired cyclone boiler showed a 48% reduction in NO_x emissions.

Pattern firing can only be applied to a boiler with multiple cyclones in stacked configuration. The technique is based on use of different air-to-fuel ratios for the stacked cyclones in such a way as to produce a staged effect. Using this technique 21% to 24% reduction in NO_x emissions was achieved in a residual-oil-fired unit. At the same time the level of O_2 in the stack increased from 1.3% to 1.6%, a 23% increase.

Staging has been shown to reduce NO_x emissions to a limited extent, but long-term test data are not available. Sustained operation of cyclones in a reducing atmosphere can cause catastrophic failure due to tube corrosion. For these reasons the cyclone boiler developer (B&W) does not recommend staging as a viable method of NO_x reduction.

OTHER METHODS

Additional efforts have been made to investigate cyclone boiler operations in which more than one combustion modification technique was applied.

None of these efforts reduced the NO_x level enough to meet NO_x emission standards.

The same is true for switching fuels. As indicated by baseline emission data none of the fuels fired in the cyclone furnace can meet existing NO_x standards. Consequently, fuel switching in itself does not appear to be a promising solution.

The final report on this study was published by EPA in January 1977. This report, entitled "Applicability of NO_x Combustion Modifications to Cyclone Boilers (Furnaces)," EPA-600/7-77-006, is available from NTIS as PB 263960/AS.

SECTION 5

CONCLUSIONS

All attempts to date to modify cyclone furnace combustion by methods including low excess air firing, load reduction, staging, and switched fuel firing have failed to reduce NO_x emission level sufficiently to meet the EPA's NO_x New Source Performance Standards for any type of fuel.

TABLE II. FULL LOAD BASELINE NO_x EMISSIONS

Fuel	NO_x emissions, dry 3% O_2 basis, ng/J	NO_x NSPS, dry 3% O_2 basis, ng/J	Reduction needed to meet the NSPS, %
Bituminous coal[a]	576 to 718	301[b]	48 to 58
Subbituminous coal[a]	546		
Lignite[a]	241 to 355	258	11 to 27
Residual fuel oil[a]	217 to 318	129	41 to 59
Natural gas[c]	208 to 323	86.0	59 to 74

[a] 1 vppm = 0.6 ng/J was assumed.

[b] Not available.

[c] 1 vppm = 0.5 ng/J was assumed.

TABLE III. NO_x EMISSIONS FROM A LIGNITE FIRED HEATER UNDER LOW EXCESS AIR CONDITIONS[a]

O_2 in flue gas, %	NO_x, dry 3% O_2 basis, ng/J	ppm
6.6	311	[c]
5.6	305	[c]
5.1	353	[c]
4.3	337	[c]
4.0	302	[c]
3.3	360	10
3.0	395	12
2.9	325	12
1.6[d]	318	11

[a] Data courtesy of the Research-Cottrell Company.

[b] Data reported in ppm, conversion factor of 1 ppm = 0.6 ng/J was assumed.

[c] Not available.

[d] Low excess air required supplemental oil to maintain ignition.

TABLE IV. NO_x EMISSIONS FROM OIL-FIRED BOILERS

Excess air level	Average flue gas measurements[a]		
	O_2, %[b]	NO_x, dry 3% O_2 basis ng/J	CO, 3% O_2 basis, vppm
Boiler A			
Normal	1.3	254	57
Intermediate	1.1	228	74
Low[c]	0.5	161	1,523
Boiler B			
Normal	2.2	206	85
Low	1.6	181	231

[a] Flue gas measurements made on composite gas samples from three individual sampling tubes. Measurements shown are averages of three analyses from three sampling tubes (short, medium, and long) for each of four probes.

[b] Boiler O_2 meter.

[c] Excessively high CO emissions at this condition.

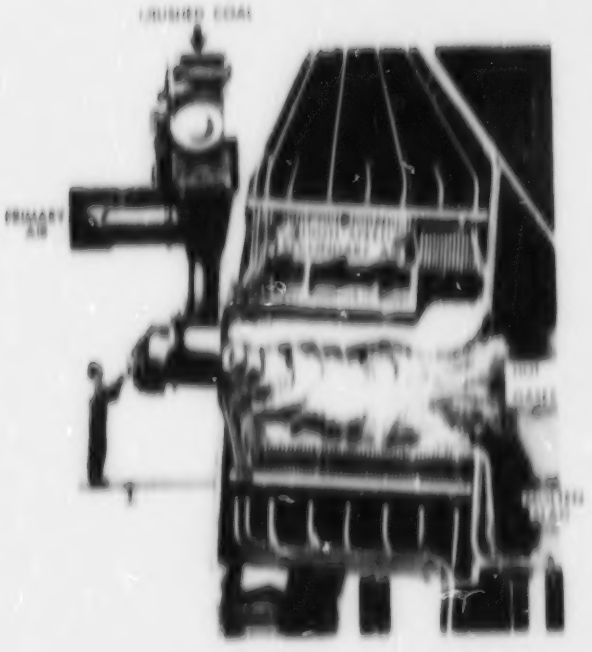
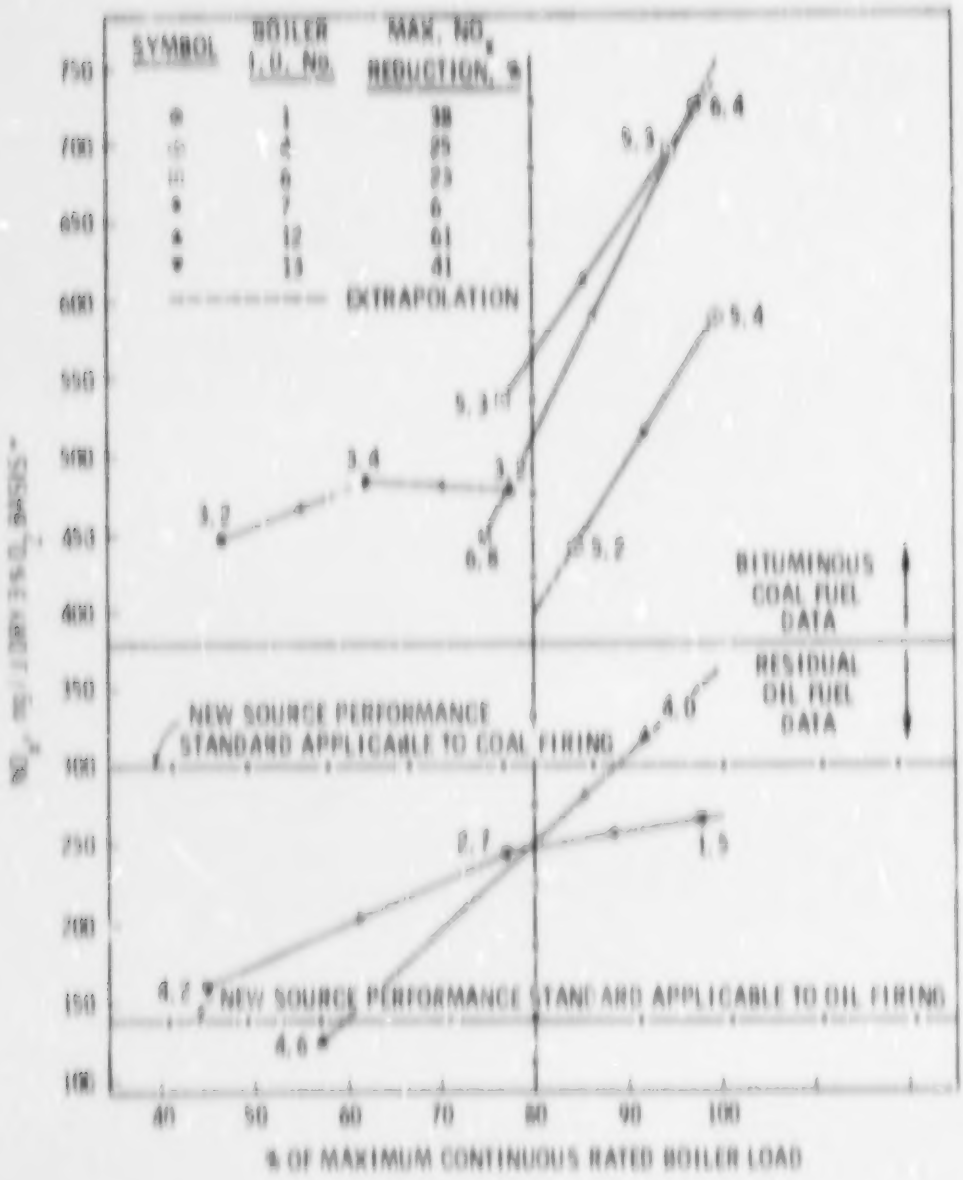


Figure 1. Cyclone furnace side view.



* 1 vppm = 0.6 ng / J

Figure 2. Overall reduction of NO_x emissions for four coal- and two oil-fired cyclone furnace boilers using load reduction (stack $\%$ O_2 levels indicated adjacent to data points).

STATISTICAL ASPECTS OF CORROSION FROM STAGING COMBUSTION IN A WALL COAL-FIRED UTILITY BOILER

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NONCATALYTIC REDUCTION OF NO_x WITH NH_3

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ABSTRACT

Exxon Research and Engineering Company has developed a post-flame injection process for the reduction of NO_x to nitrogen with ammonia (U.S. Patent No. 3,900,554). The feasibility of this technique has been demonstrated by ER&E and Exxon's Japanese affiliate for an oil fired boiler. The technology has been commercialized for oil and gas fired boilers. The ammonia injection technology (Thermal DeNO_x process) is viewed as potentially a useful supplement to available combustion modification techniques for attaining low NO_x levels for installations that require such degree of control.

An analysis of utility boiler types will be made to determine what coal fired boiler types by design, size, or manufacturer are most likely to be amenable to the Thermal DeNO_x process. Budget type cost analysis for the application of the Thermal DeNO_x process will be made as a function of utility boiler size, fuel, appropriate boiler characteristics and degree of NO_x reduction. The costs of the Thermal DeNO_x process will be compared with those for extreme combustion modifications that would be required to achieve very low NO_x levels.

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SECTION 1

INTRODUCTION

Exxon Research and Engineering Company has developed a new process called Thermal DeNO$_x$ for reducing emissions of oxides of nitrogen from large stationary combustion sources. This non-catalytic process is based on the selective reduction of NO$_x$ with NH$_3$ in the homogeneous gas phase (1,2). The Thermal DeNO$_x$ process has been commercially demonstrated in gas and oil-fired steam boilers and process furnaces, and tests have also been conducted on a municipal incinerator. Exxon Research and Engineering Company has granted licenses on this process in Japan where NO$_x$ emission regulations are very stringent.

The Thermal DeNO$_x$ process involves injection of ammonia into the hot flue gas within a narrow and critical temperature range. In the first full-scale commercial demonstration, conducted in 1974 at Tonen Sekiyu Kagaku K.K.'s Kawasaki Plant, a reduction in NO$_x$ emissions of up to 70 percent was achieved on a 70-ton-per-hour oil-fired steam boiler. Although the temperature sensitivity will cause the reaction's effectiveness to vary from one installation to another, the NO$_x$ reduction is essentially independent of the concentration of oxides of sulfur or particulate matter in the flue gas. The specific level achievable is dependent upon a number of factors, including the heater design, operating mode, and initial NO$_x$ level.

Thermal DeNO$_x$ may be applied to boilers for additional NO$_x$ reduction after combustion modifications such as staged firing or flue gas recirculation have been implemented. As Thermal DeNO$_x$ is a post-flame injection process, it is not affected by certain limitations imposed on combustion modifications, e.g., by reduced boiler load capability in retrofit applications. Thus, the Thermal DeNO$_x$ process is viewed as an effective supplement to available combustion modification techniques for attaining low NO$_x$ levels for combustion installations that require such high degree of emission control.

In the present paper, the technical background of Thermal DeNO$_x$ is reviewed and the objectives of a pending contract between Exxon Research and Engineering Company and the U.S. Environmental Protection Agency on the application of this process to coal fired utility boilers are discussed.

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SECTION 2

CHEMISTRY OF THE PROCESS

The process chemistry relies on the selective reaction between NH_3 and NO_x to produce nitrogen and water. This reaction proceeds in the presence of excess oxygen within a critical temperature range. The overall NO reduction and production reactions are summarized in equations (1) and (2), respectively:

$$NO + NH_3 + 1/4\ O_2 \rightarrow N_2 + 3/2\ H_2O \quad (1)$$

$$NH_3 + 5/4\ O_2 \rightarrow NO + 3/2\ H_2O \quad (2)$$

In typical flue gas environments, the NO_x reduction shown as equation (1) dominates at temperatures around 950°C (1740°F). At higher temperatures, the NO_x production reaction shown as equation (2) becomes significant, and it dominates at temperatures over about 1000°C (1830°F). As temperatures are reduced below about 900°C (1650°F), the rates of both reactions slow, and the ammonia flows through unreacted. These effects of temperature on NO_x and NH_3 concentrations are shown in Figure 1.

The following chain reaction cycle was proposed by Lyon (2) for the NH_3-NO-O_2 reaction system:

$$NH_2 + NO \rightarrow N_2 + H + OH \quad (3)$$

$$NH_2 + NO \rightarrow N_2 + H_2O \quad (4)$$

$$H + O_2 + OH \rightarrow O \quad (5)$$

$$O + NH_3 \rightarrow OH + NH_2 \quad (6)$$

$$OH + NH_3 \rightarrow H_2O + NH_2 \quad (7)$$

$$H + NH_3 \rightarrow H_2 + NH_2 \quad (8)$$

This chain reaction mechanism is sufficient to explain qualitatively the observed reduction of NO by NH_3 in the presence of O_2.

Exxon's technology also includes means of altering the utilizable temperature range. The addition of H_2 shifts the temperature window to lower levels, as shown in Figure 2. It should be noted that hydrogen does not widen the

temperature range, but merely changes it. The magnitude of this shift is mainly a function of the amount of H_2 injected relative to the NO_x. At H_2/NO_x ratios on the order of 2:1, the NO_x reduction reaction can be forced to proceed rapidly at 700°C (1290°F). By judiciously selecting the H_2/NO_x injection ratio, flue gas treatment can be accomplished over the range of 700-1000°C.

The same effect produced by H_2 can also be provided by other combustible gases, such as hydrocarbons or carbon monoxide. Use of these additives for temperature control, however, is not generally recommended because of the possible formation of undesirable by-products such as small amounts of hydrogen cyanide.

In addition to temperature, the process is also sensitive to initial NO_x and NH_3 concentrations. The NH_3 injection rate is generally expressed as a mole ratio relative to the initial NO_x concentration. The reductions obtained with various initial NO_x levels are shown as functions of this parameter in Figure 3.

Other variables affecting performance are excess oxygen and available residence time at the reaction temperature. Minimizing excess air tends to enhance the NO_x reduction, as does maximizing residence time.

The issue of possible pollutant by-products (HCN, N_2O, CO, SO_3 and NH_4HSO_4) was addressed by Exxon Research studies [3]. As mentioned before, HCN can be produced only if hydrocarbons are present in the Thermal DeNO_x reaction zone. Under normal conditions, hydrocarbons are absent from this zone. As regards N_2O production, it represents only one to two per cent of the NO_x reduced [1,3]. The Thermal DeNO_x process does not generate CO by reducing CO_2. However, CO oxidation is inhibited by NH_3, so that if CO is present, it would be emitted unreacted into the atmosphere. This effect is of no consequence under normal operating conditions for oil and gas fired boilers, as CO oxidation is complete before the NH_3 injection point.

Detailed laboratory experiments have shown no interaction between the Thermal DeNO_x process and sulfur compounds in the high temperature flue gas regions. That is, sulfur or its oxides do not interfere with the NH_3-NO_x-O_2-H_2 chemistry. Additionally, ammonia injection has been shown to cause neither additional homogeneous nor additional heterogeneous oxidation of SO_2 to SO_3.

To the extent that the thermal reduction of NO leaves some NH_3 unreacted, and as the combustion gases cool, NH_3 reacts with SO_3 and H_2O to form ammonium sulfates. (Ammonium bisulfate is a corrosive liquid at air heater temperatures.) Based on laboratory and commercial tests, these sulfates do not create either severe corrosion or unacceptable air heater fouling problems when Thermal DeNO_x is used in accordance with its design specifications. Long term tests conducted in two oil-fired boilers by Tonen Sekiyu Kagaku K.K. in Kawasaki, Japan, revealed these deposits could easily be removed by waterwashing the air heaters at reasonable intervals.

SECTION 4

ENGINEERING CONSIDERATIONS

When applying the Thermal DeNO$_x$ process to commercial equipment, performance is generally limited by the extreme temperature sensitivity of the reaction and its dependence on the local concentrations of reactants, NH_3, NO_x, O_2, and H_2. The Exxon technology provides a means of adapting the chemistry requirements to industrial equipment environments, and NO_x reductions up to about 70% can often be achieved by the use of Thermal DeNO$_x$ technology in existing boilers. Application to new, grass-roots designs is usually easier because the internal configuration of the high temperature zone can be adjusted to complement the process demands.

The Thermal DeNO$_x$ process utilizes proprietary Exxon gas phase mixing technology to rapidly and efficiently mix the small volume of reagents with the hot flue gas. Correct distribution of reactants is required because of non-linearities in the reaction rates. Locally high concentrations of NH_3 will decrease the maximum attainable NO_x reduction and will also result in the breakthrough of unreacted ammonia.

Accommodating flue gas temperature variations is important if high DeNO$_x$ rates are to be achieved. Not only does the system have to accommodate flue gas temperature changes caused by normal load and operating variations, but it also must allow for fluctuations across the reaction zone caused by non-uniformities in flow and heat transfer. It follows, therefore, that a case-by-case evaluation of flue gas temperatures and local conditions is required for the application of thermal DeNO$_x$ for each installation considered.

SECTION 4

PROCESS COSTS

The costs associated with the Thermal DeNO$_x$ process are sensitive to the particular circumstances of the application. Factors influencing cost include initial NO$_x$ concentration, reduction target, compatibility of the heater design and operation, and local price and availability of chemicals and utilities.

As an example, consider applying the process to a 100 MWe oil-fired utility plant with an initial NO$_x$ level of 225 ppm (about 0.3 lb. NO$_x$/M Btu fired). Assume the boiler geometry and operating conditions provide a temperature in the reaction zone which does not require H$_2$, and that for a 50% NO$_x$ reduction target, an approximate NH$_3$/NO$_x$ injection ratio of 1.0/1 is feasible. Thus, Thermal DeNO$_x$ will have the following estimated operating costs:

(a) NH$_3$ @ 1.0 mole per mole NO$_x$ (assume 170 $/ton) = 0.9 ¢/M Btu

(b) Utility air @ 210 SCF per M Btu fired (assume 0.005 ¢/SCF, including compressor cost) = 1.0 ¢/M Btu

The total operating cost is estimated at 1.9 ¢/M Btu.

Note that 20 psig utility air is used as a diluent in the injection system. An alternative approach would be to use a similar quantity of low pressure steam, resulting in a different operating cost.

The availability of chemicals and utilities usually represents the greatest variable in the installation cost. In situations where such facilities are already available on site, the equivalent cost for capital investment for a large utility boiler can be as low as about 1 ¢/M Btu (assuming annual charges for finance, maintenance, and depreciation total 20% of investment).

The equivalent cost for the above example totals about 2.9 ¢/M Btu fired. With the assumed reduction of NO$_x$ emissions from 225 to 112 ppm, the cost-effectiveness is about 190 $/ton of NO$_x$ removed (expressed as NO$_2$). As previously stated, total cost and effectiveness will vary for other cases depending on both technical and economic factors. Where higher DeNO$_x$ severities are required, or where optimum flue gas temperatures are not available, H$_2$ and higher NH$_3$/NO$_x$ ratios would be required, thus significantly increasing overall cost.

SECTION 5

COMMERCIAL SCALE EXPERIENCE

Thermal DeNO$_x$ has been demonstrated in six commercial boilers and furnaces to date. Actual capability often represents a compromise between the technical limits of the process chemistry and cost-effectiveness. In many situations, performance is maximized at full load operation, and smaller NO$_x$ reductions accepted at reduced loads resulting in lower reaction zone temperatures. In such installations, total NO$_x$ emissions are generally at target levels over the full range of operating conditions because of the reduced NO$_x$ production at lower loads. Results from all six demonstrations are shown over their range of operating conditions as a function of flue gas temperature in Figure 4.

SECTION 6

APPLICATION OF THERMAL DeNO$_x$ TO COAL FIRED UTILITY BOILERS

At the time of writing this paper (June 29, 1977), a contract is being negotiated between Exxon Research and Engineering Company and the U.S. Environmental Protection Agency on the Thermal DeNO$_x$ process. The purpose of this pending contract will be to evaluate and document the feasibility of Exxon Research's proprietary Thermal DeNO$_x$ process to coal fired utility boilers for reducing NO$_x$ to nitrogen. A program consisting of four task elements is envisioned for this contract. These tasks are as follows:

Task 1. The Thermal DeNO$_x$ process technology will be documented with relevant background information and data. The data and information generated by Exxon Research in the development of the Thermal DeNO$_x$ process will include those resulting from bench scale laboratory experimentation; development test data obtained with an oil fired boiler and with a gas fired test furnace; and commercial scale test data obtained at Exxon's affiliate's Kawasaki plant on an oil fired steam boiler.

Task 2. A broad analysis will be made of utility boiler types to determine if certain boiler types by design, size, or manufacturer, are more amenable to Thermal DeNO$_x$ than others. This analysis will be made based on information available on the current population of coal fired utility boilers in the U.S.

Task 3. Budget type cost analysis will be made of the Thermal DeNO$_x$ process as a function of utility boiler size, fuel, appropriate boiler characteristics and degree of NO$_x$ reduction desired. This analysis will include cost components of engineering, capital investment, and operating costs. Key cases to be considered for coal fired utility boilers are (a) trimming NO$_x$ emissions to meet the current NSPS of 0.7 lb./10^6 Btu on coal fired boilers unable to meet the standard with state-of-the-art combustion modification techniques; and (b) further reduction in NO$_x$ emissions to the 0.1-0.4 lb./10^6 Btu range.

As part of the budget type cost analysis effort, a comparison will be made of the costs of the Thermal DeNO$_x$ process with that of extreme combustion modifications that would be required to achieve very low NO$_x$ levels for coal fired units.

Task 4. Without reimbursement by EPA, ER&E will conduct a laboratory scale test program to test the effectiveness of the Thermal $DeNO_x$ process for coal firing. The effects of Thermal $DeNO_x$ on NO_x, SO_2, SO_3, HC, CO, HCN, NH_3, and particulates (including sulfate and nitrate particulates) will be determined. Relevant results of this laboratory scale test program will be made available to EPA as part of the pending contract for their evaluation of the results.

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1. Lyon, R. K., "Method for the Reduction of the Concentration of NO in Combustion Effluents Using Ammonia," U.S. Patent 3,900,554, August 19, 1975.

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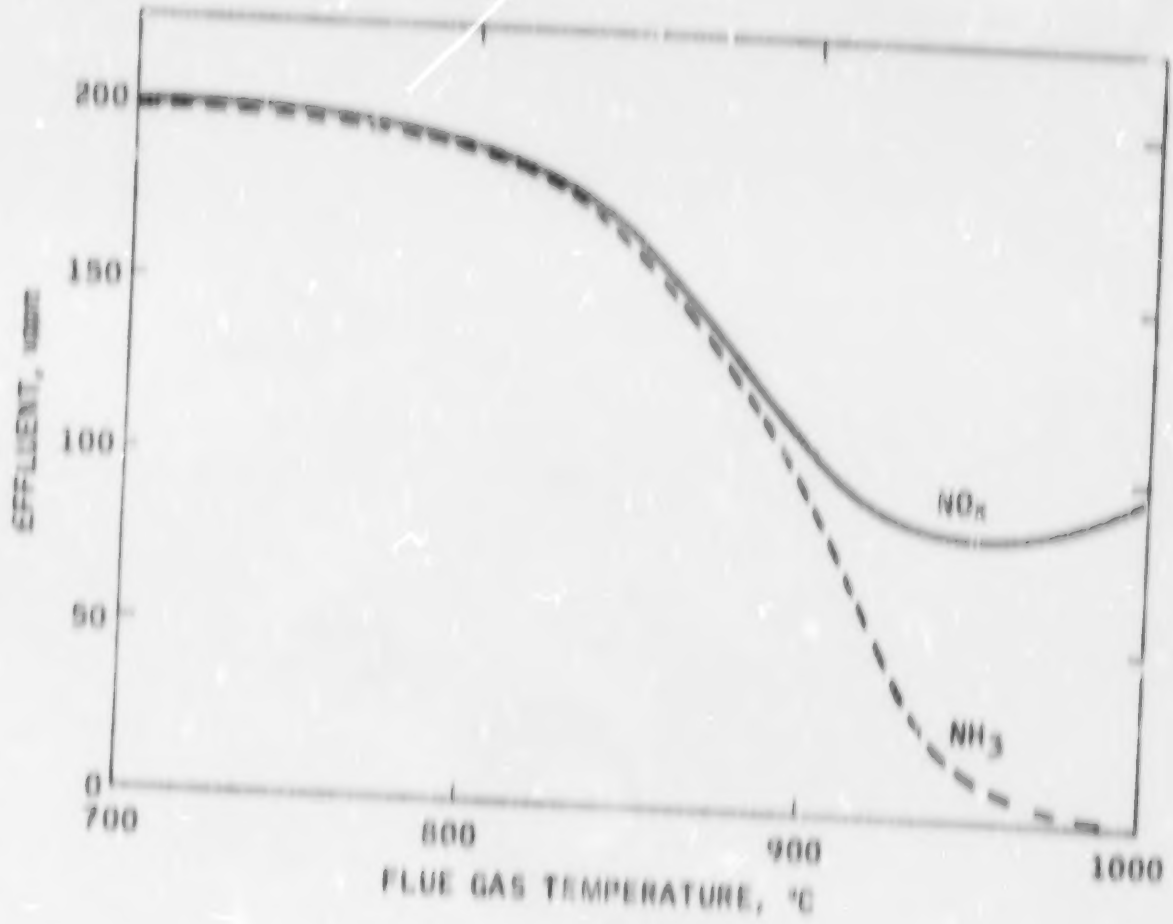

Figure 1. Thermal DeNO$_x$ reaction products as functions of temperature without hydrogen.

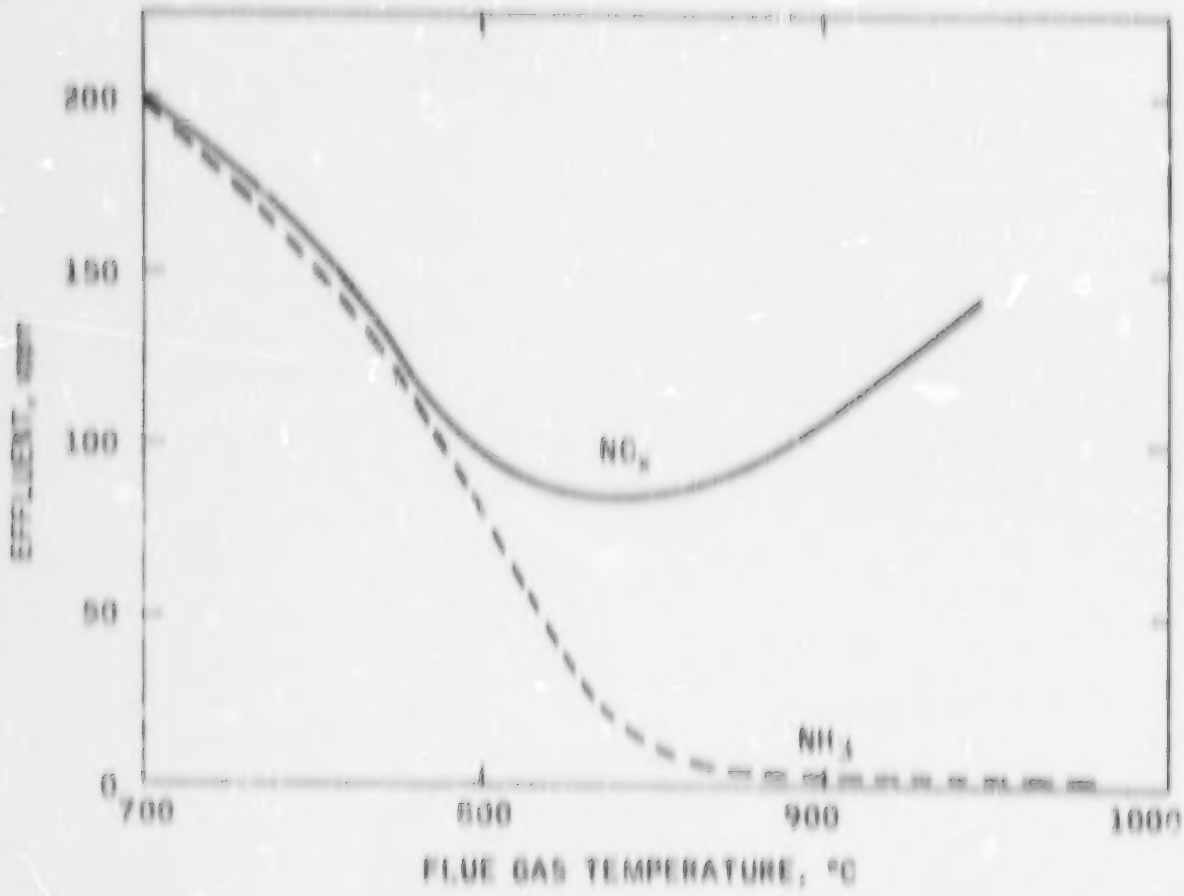

Figure 3. Thermal DeNO$_x$ reaction products as functions of temperature with hydrogen added.

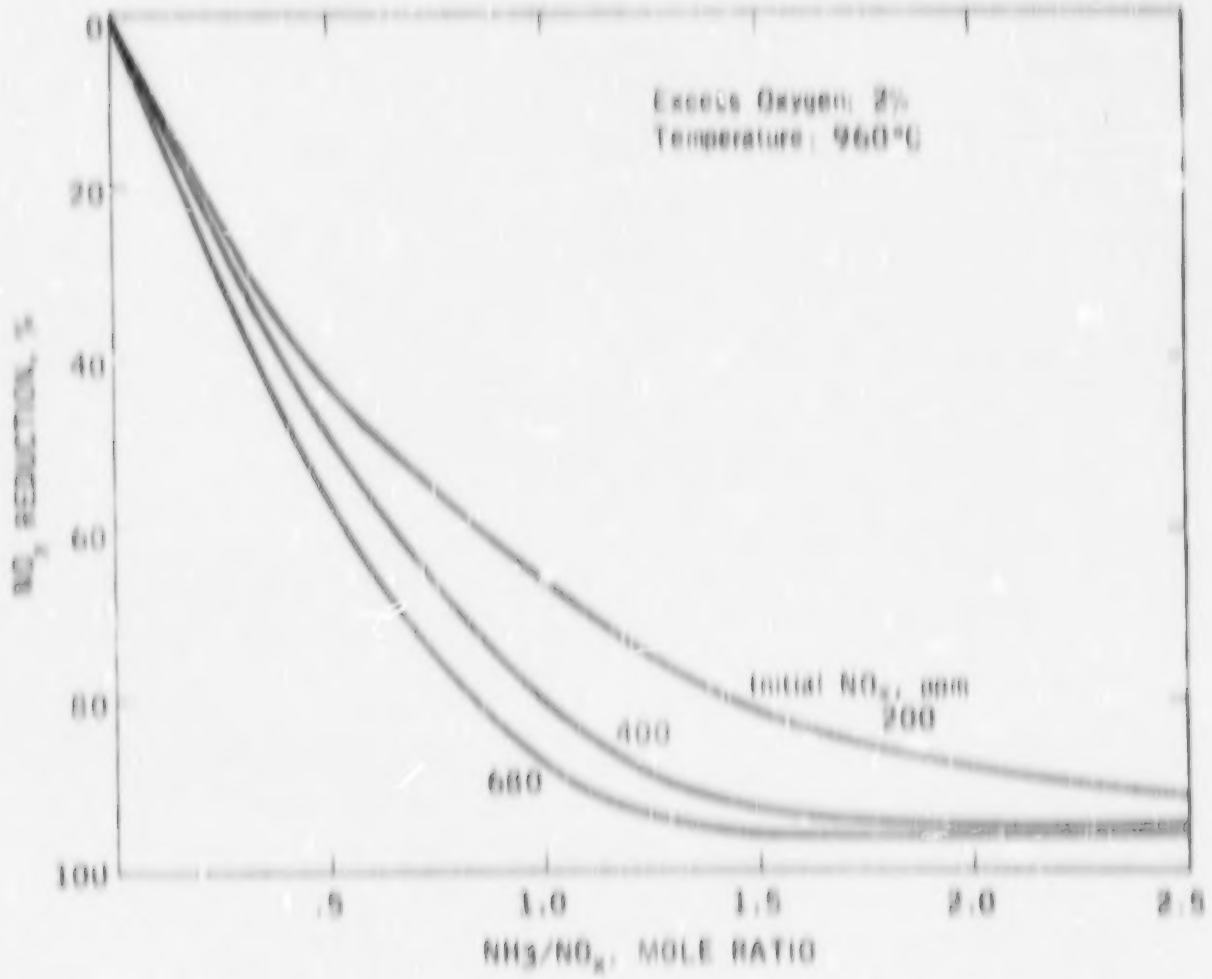

Figure 1. NO_x reduction as a function of NH_3 injection ratio.

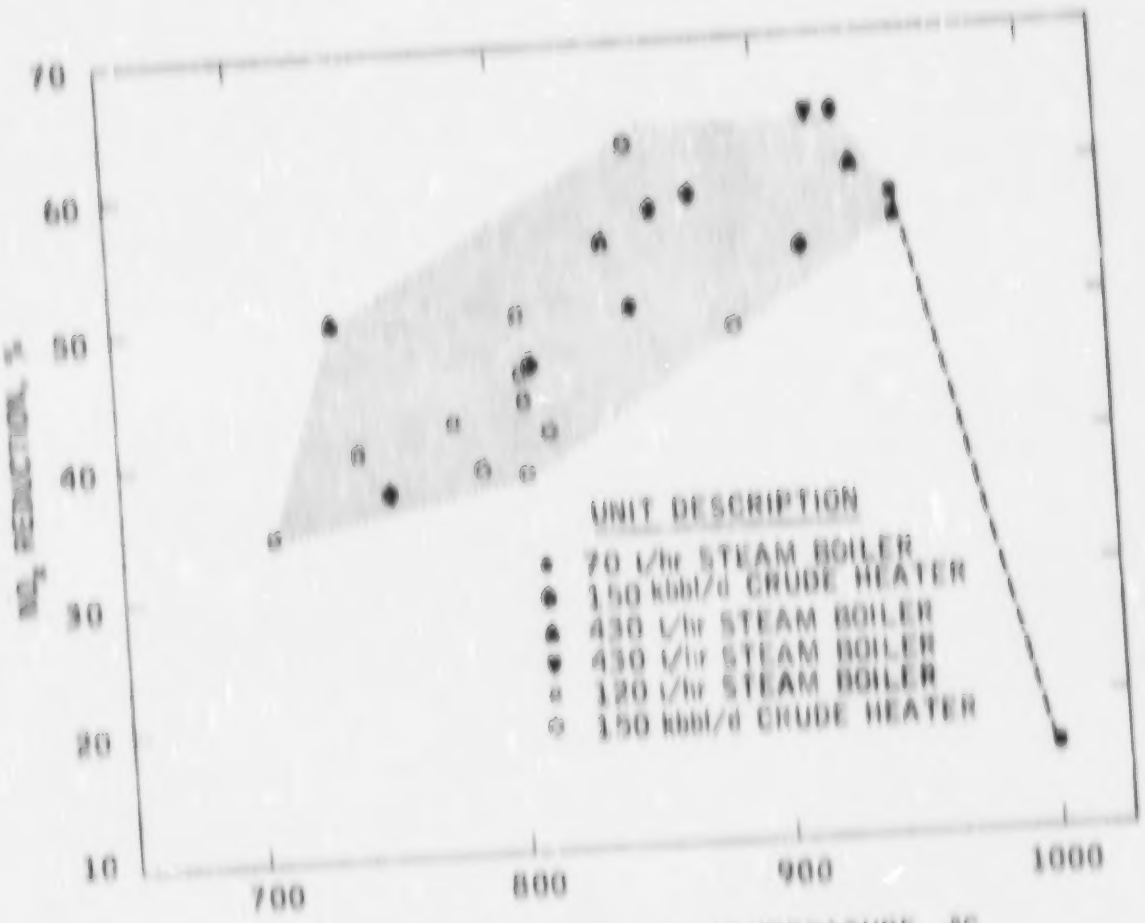

Figure 4. Performance of Thermal DeNO$_x$ systems in commercial applications.

WESTERN COAL USE IN INDUSTRIAL BOILERS

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WESTERN COAL USE IN INDUSTRIAL BOILERS

ABSTRACT

Ten small and intermediate-sized (4.5 Mg/hr to 113 Mg/hr (10,000 lb/hr steam to 250,000 lb/hr steam)) coal-fired boilers in the upper Midwest have each been tested on both a bituminous eastern coal and a subbituminous western coal.

The purpose of this study was to determine the feasibility of substituting western subbituminous coal for eastern bituminous coal as a means of reducing the SO_2 emissions from this class of boiler and to demonstrate the feasibility of greatly expanded western coal utilization as a means of reducing the use of oil and gas.

The scope of this study was such that the representative boiler types were tested on both eastern and western coal for a period of time sufficient to completely characterize their individual emission and operational characteristics.

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DISCLAIMER

This report has been reviewed by the National Environmental Research Center, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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SECTION 1

INTRODUCTION

Faced with the problem of complying with sulfur dioxide control regulations, electric utilities and industries in the Midwest have been increasing their use of low-sulfur western coal. The extent to which Midwestern demand for western coal will continue to increase depends on a number of factors. Foremost among these are: (1) the evolution of federal, state, and local sulfur dioxide control regulations; (2) the growth of coal as a boiler fuel; and (3) the cost of western coal relative to the costs of alternate fuels and control technologies.

The upper Midwest region (Minnesota, Wisconsin, Iowa, Nebraska, and Illinois) is presently an area where low-sulfur western subbituminous coal is most competitive with midwestern and eastern coals. Within this region, there is considerable variation with regard to western coal use versus the traditional eastern supply. This variability is due in part to equipment limitations which dictate that a certain coal be burned.

For this reason it is necessary to determine the operational compatibility of western coal with existing industrial coal-fired equipment, if fuel substitution is to be considered a viable alternative sulfur oxides control strategy.

The purpose of this program, the test results of which are detailed in this paper, was to assess the effectiveness of the use of lower sulfur western coals as a means of reducing sulfur oxides emissions from industrial-sized boilers in the size range 4.5 to 111 Mg/hr (10,000 to 250,000 lb/hr steam). The impact on SO_x, NO_x, CO, particulates, and unburned hydrocarbon emissions has been assessed as a consequence of this fuel conversion.

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The scope of the testing program included testing ten representative types of coal-fired industrial boilers for a period of one month each on eastern and western coal. During this testing period, the pollutant emissions listed above were measured both in a baseline configuration and in an optimized firing mode. Operational problems of the unit were characterized for each coal. Potential reductions of pollutant emissions have been estimated for each unit type and each coal tested.

SECTION 2

PROPERTIES OF WESTERN SUBBITUMINOUS COALS

A large supply of low sulfur, subbituminous coal exists in the Powder River region of Wyoming and the Fort Union region of southeast Montana. This coal is being mined at a rapidly increasing rate. One mine in Wyoming, for example, increased production from 0.09 million tons per year in 1973 to 1.1 million tons per year in 1974, a factor of 3.7 in only one year. However, the most impressive statistics are the reserve capacity of these western coal fields. That same mine in Wyoming whose production increased so dramatically in 1974 has a reserve capacity of 16.5 billion tons. This translates to a lifetime of 50 years at current production rates. The large reserves, coupled with the relative ease of strip mining, point to a ready supply of coal for fuel if other constraints are met. One of these constraints is the subject of this paper.

The compatibility of these western subbituminous coals with existing industrial boilers could be a hinderance to their wide acceptance as a boiler fuel. The compatibility of coal and boiler are determined both by coal properties and boiler design. Since the boiler designs are fixed in existing units, the coal properties are the variables of interest.

Western coal characteristics are those of a typical subbituminous coal: an ash-free higher heating value of 19 to 24 MJ/kg (8,200 to 10,500 Btu/lb), and a high moisture content of 20% to 30%. The ash content of most of these coals is less than 10% by weight. The western subbituminous coals exhibit high volatile to fixed carbon ratios, typically approaching a value of one. The coals tested during this study are presented in Table 1. The mineral analysis is also included for selected coals. The sequence number keys the ultimate analysis with the mineral analysis.

The western subbituminous coals are also classed as "free-burning" coals. In the free-burning coals, the pieces do not fuse together, but burn separately or, after fusion, the mass breaks up quickly into fragments. This characteristic causes problems in certain types of stokers where there is inadequate control of undergrate air distribution.

The high moisture content of the western coals causes the greatest combustion difficulty in industrial-sized equipment. In most units with superheaters, it leads to high steam superheat temperatures. It also causes flame stability problems in pulverized coal combustion and ignition problems in stoker-fired units. In order to recover the lost steam capacity, some pre-drying of western coals will be necessary for firing in units designed for eastern coal.

The second major problem with western coal is the size distribution of the delivered coal. Most western coals do not travel or weather well. The coal has a tendency to break into fine sizes while in transit. Therefore, even if the coal has been sized before shipment, the as-received coal will exhibit a change in size distribution toward the smaller sizes. This shift becomes more severe with longer transit and/or storage periods. The effect of this coal property on stoker unit performance is discussed below.

This paper is divided into a discussion of pulverized coal firing and stoker firing of both eastern and western coal. A general overview of boiler performance is presented in Table II. Here, the units tested are rated in terms of emissions, efficiency, and overall ease of operation. The type and source of the coals tested are also given for each boiler.

SECTION 1

PULVERIZED COAL COMBUSTION

Unit No. 3, a pulverized coal-fired boiler, was tested at Dairyland Power Cooperative at the Alma, Wisconsin generating station. This four-burner face-fired unit manufactured by Riley Stoker Corporation is rated at 104.3 MJ/hr (330,000 lb/hr) steam flow. The coal is pulverized with two ball tube mills, one mill for the upper two burners and one for the lower two burners. The unit is equipped with a spray steam attemperator. Fly ash collection is accomplished with a UOP-designed cold-side electrostatic precipitator (ESP).

The two fuels used during the testing were:

Eastern Base coal

- 4% sulfur
- 10% ash
- 24 MJ/kg (10,500 Btu/lb)
- 19% volatiles

and

Montana Coal

- 0.7% sulfur
- 12% ash
- 19.5 MJ/kg (8,400 Btu/lb)
- 37% volatiles

BOILER PERFORMANCE - ALMA UNIT NO. 3

The boiler performed well on both coals, although the unit was limited in maximum load due to excessive superheat steam temperature on the Montana coal. The steam attemperation system was not adequate to reduce the temperature to the desired 755 °K (900°F) level at loads above 78.3 MJ/hr (174,000 lb/hr) steam on western coal. This compares to a maximum load of 92.3 MJ/hr (204,000 lb/hr) steam on eastern coal. The boiler is design rated at 104.3 MJ/hr (230,000 lb/hr) steam, however, this load is no longer achieved.

The primary factor causing the excessive steam temperature is the high moisture content of the coal. The water reduces the flame temperature which in turn reduces the radiant heat flux to the water walls, resulting in lower steam generation. This lower heat transfer (a function of temperature to the fourth power) removes less heat in the radiant section; however, the gas still contains a large enthalpy which then acts on a decreased amount of steam in the convective section, resulting in increased steam temperatures. The water in the fuel also results in greater gas flows which increase heat transfer rates in the convective pass.

The excessive steam temperature problem is a function of boiler design. For example, a boiler designed for western coal might not be able to make design steam temperature on eastern coal.

Increased steam attemperation would result in full capacity operation on western coal.

PULVERIZER MILL PERFORMANCE

Eastern coking coals, when exposed to furnace temperatures, will swell and form lightweight, porous coke particles. These may float out of the furnace before they are completely burned. As a result, carbon loss will be high unless pulverization is very fine. Free-burning (western) coals, on the other hand, do not require the same degree of fineness because the swelling characteristic is absent.

High volatile (western) coals ignite more readily than those with a low volatile content. Therefore, they do not require the same degree of fine pulverization. With the exception of anthracite, however, the low-volatile coals are softer, and therefore have a higher grindability. As a result, mill capacity is greater at increased fineness than with high volatile coals (Ref. 1).

Table III shows the action analyses and the loads of the coal burned in tests 9, 16, 57, 61, 75, and 78. Tests 9 and 16 were on eastern coal. Test 16 was with one mill out of two operating so the load in the mill was

the same as it would have been with both mills operating at 47.2 Mg/hr (104,000 lb/hr) steam. The screen analyses of tests 16 and 78 may then be compared. It is seen that the western coal did not grind quite as well as the eastern coal. However in the opinion of de Lorenzi (Ref. 1), free-burning coals need not be ground as finely as coking coals, and this was not thought to be a severe problem. An equally important factor in mill grinding capacity is moisture. From Reference 1, frequently too much emphasis is placed on grindability, while other factors such as moisture, which also affect mill capacity, are almost entirely overlooked. The capacity of a pulveriser is not directly proportional to the grindability of a coal. Correction must be made for variation in fineness and moisture content.

Without quantitative analysis, it can be seen in Table III that the moisture content of test 78 is a factor of eight times higher than test 16. The grindability of the other tests tend to follow the moisture content. Test 57 with the highest moisture content exhibited the poorest grindability, followed by tests 75, 73, 78, and 61 in order of increasing grindability.

The poorly pulverized coal burns more slowly resulting in lowered heat transfer in the near-flame region (radiant section) and increased heat transfer to the convective section. At high loads (tests 57 and 75), the poor grind probably contributed to the excessive superheat steam temperature problem.

EMISSIONS FROM AIMA UNIT NO. 1

A coal performance comparison for Aima Unit No. 1 is presented in Table IV. In this table, western coal (test 66), is compared to the nearly identical eastern coal (test 9).

Significant differences in coal performance are noted for:

- SO_x emissions
- NO emissions
- Carbon carryover
- Uncontrolled particulate emissions
- Unit efficiency

For the first four items, the western coal performed better than the eastern coal. Sulfur oxides emissions were reduced by a factor of 3 by substituting western coal. At the same time nitric oxide emissions were reduced 24% and carbon carryover was virtually eliminated. Uncontrolled particulate loadings were reduced 11%. The performance of the ESP was not affected by the fuel switch; it continued to operate at 99+% efficiency. Carbon monoxide and unburned hydrocarbon emissions were generally less than 100 ppm each. In the optimum furnace configuration, these emissions are controlled by excess air. Below 1% excess O_2 in the flue gas, these emissions became significant. Soot formation, resulting in a "black stack" was also a problem below 1% excess O_2. However, boiler efficiency was lower on western coal due to high moisture losses resulting from fuel-contained water.

DISCUSSION

Figure 1 is a plot of nitric oxide as a function of excess O_2 in the flue for western coal at four loads. Figure 2 contains the same type data for the base eastern coal. Both figures show increasing NO with increasing O_2 at a constant load; however, the absolute magnitude of NO emissions from western coal is less at any given load and O_2 level. Most of the NO data on Figure 1 fall below the EPA limit for new coal-fired units of 0.7 lb of NO_x at NO_2 per million Btu (about 300 ppm). Attempts to reduce the NO emissions of the eastern coal to these same (less than 300 ppm) levels resulted in high CO emissions.

Included in the factors that influence NO emissions are:

- Flame temperature
- Fuel nitrogen
- Excess oxygen

All three of these influence NO emissions when switching to western coal. The temperature of the western coal flame is lower than the eastern due to the high moisture content of the coal resulting in lower NO emissions from atmospheric nitrogen fixation and to a lesser extent fuel nitrogen conversion. In general the western coal could be fired at lower excess air before combustible losses became a problem. This is due to the higher ratio of the volatile matter

to fixed carbon content of the western coal which results in less solid carbon to be burned out in the post-flame gases. The lower excess air requirements result in lower NO emissions.

Table V contains data for all coals tested which show that the fuel nitrogen content of the western coal is generally lower than eastern coal. In any case, not all of the fuel nitrogen present in coal is converted to nitric oxide. Typically, only 40% to 60% is converted with the amount dependent on coal type, fuel nitrogen content, firing conditions, and the structure of the nitrogen-containing molecule within the coal.

The substitution of western coal for eastern coal results in an 11% reduction in NO emissions on the average. The western coals used in this comparison had 18% less fuel-bound nitrogen than the eastern coals. The emission comparisons were based on western and eastern coal tests at comparable loads and excess O_2 levels. Since NO_x arises from both conversion of fuel-bound nitrogen and fixation of atmospheric nitrogen, it is difficult to draw any correlation between fuel nitrogen content and NO_x emissions. This is further influenced by the fact that different coals have different types of nitrogen-containing molecules which, depending on their structure, are more or less easily oxidized to NO in the flame.

The conversion of fuel nitrogen to NO is a function of the structure and distribution of the nitrogen-containing molecules within the coal. For example, under certain conditions it could be important if the nitrogen containing molecules are associated with the volatile fraction of the coal rather than the fixed carbon portion. The chemical oxidation state of the nitrogen species in coal is important since nitrogen that is partially oxidized will be more easily converted to NO. For example, azide groups (N_3) will more readily be reduced to N_2 than $-NO_2$ groups which will be more easily oxidized to NO under flame conditions.

Figure 3 compares the NO emission behavior as a function of excess O_2 for three western coals on two pulverized coal units. The Fremont data were taken on a 73 MJ/hr (160,000 lb/hr) four-burner boiler while the Alma data came from a 104 MJ/hr (230,000 lb/hr) four-burner unit. These data

indicate that the NO emissions are unit-dependent as well as coal-dependent. Furnace volume, burner heat release rate, burner spacing, and fuel/air mixing characteristics all have been found to affect NO emissions.

In order to control SO emissions from the eastern coal, it was necessary to operate at higher O_2 levels; this led to higher NO emissions. For western coal firing, it has been shown that the furnace can operate at lower excess O_2, thus lower NO. Western coal typically contains less bound fuel nitrogen than eastern coal. This fuel nitrogen can be as little as half the amount found in typical eastern coals.

The third factor affecting NO emissions is flame temperature. The high moisture content of western coal causes the temperature of the western coal flame to be lower than the eastern coal flame. This lower flame temperature lowers the fixation of molecular nitrogen in the combustion air. The effect of flame temperature on the conversion of fuel nitrogen to NO is not well understood.

Sulfur oxides emissions are largely a function of sulfur in the fuel. There has been some work that indicates that coal ash composition may affect the amount of sulfur oxides emitted (ref. 7). The comparison of the eastern and western coals at Nine Mile Point VII shows the benefit of fuel substitution in the control of SO_x emissions.

Particulate Emissions

Table VII contains particulate emissions data from the eastern and western coals tested. The ash content of the coal and the combustible content of the fly ash emissions are given for a comparison of the maximum potential emissions from each coal. For a tangent, 13 Btu/lb (30,000 J/kg) pulverized coal boiler at 40% firing of eastern coal, approximately 6% of the coal ash injected to the fire ga stream contains only 41% of the western coal ash as found in the flue gas under identical firing conditions and for coals with the same ash content. Electrostatic precipitator efficiencies were determined by the fuel switch. Combustible losses were higher on eastern coal than on western coal. A 3% reduction in quantified particulate emissions was realized by switching to western coal.

A 4-burner, 73 MJ/hr (160,000 lb/hr) pulverized coal unit was tested at Fremont, Nebraska, on a Wyoming subbituminous coal and a Colorado subbituminous coal. Again the Wyoming coal with a higher ash content had less fly ash in the flue gas than the Colorado coal. However, the cyclone dust collector efficiency was reduced to 72% on the Wyoming coal from 80.5% on the Colorado which resulted in 110 ng/J (0.25 lb/MBtu) greater controlled particulate emissions.

SECTION 4

STOKER-FIRED BOILERS

Coal firing of industrial boilers can be separated into two broad classes -- suspension firing and grate firing.

Suspension firing is normally applied in larger sized units; however, units as small as 11 MJ/hr (35,000 lb/hr) steam have been built for pulverized coal firing. Current economics indicate a break-even point in the 31 to 111 MJ/hr (300,000 to 350,000 lb/hr) steam flow range. Suspension firing includes both pulverized coal firing (70% through a 200 mesh screen) and cyclone firing (crushed to 6.35 mm (1/4") with about 10% through a 200 mesh screen).

Grate firing comprises three general stoker types:

1. Underfed
2. Overfed
3. Spreader

Within these three types, there are a number of variations in feed methods and grate design. Stoker-fired boilers have been built covering the entire capacity range of this study: 4.5 to 111 MJ/hr (10,000 to 250,000 lb/hr) steam. The present stoker-fired boiler population represents a highly individualized array of equipment.

Table 11 presented previously lists stoker types tested in this study. From this assessment of units, the emissions and operating characteristics of western coal firing have been determined.

OPERATIONAL CHARACTERISTICS OF WESTERN COALS IN STOKERS

Two properties of western subbituminous coals result in operational problems for stoker-fired units. They are:

- Coal weathering - resulting in size reduction
- "Free burning" characteristic - resulting in an uncovered grate

Many older underfeed and traveling grate stokers were manufactured with insufficient control of the undergrate air to use western coal as a fuel. The problem is manifested when a dark spot of unburned coal develops on the grate. This patch of coal can grow into a large clinker if special measures are not taken to remove it. The "black patches" occur because there is insufficient local air pressure under the patch to maintain vigorous burning. The loss of local air pressure occurs because some other portion of the grate, in the same plenum control area, has become thin or bare and allows the combustion air to pass through easily. These units were designed for an eastern coal that formed some coke while burning and in turn maintained even coverage of the grate. The free-burning western coals, on the other hand, tend to form a fine powdery ash which either blows off or falls through the grate, leaving it bare. This problem is compounded by the serious size reduction that occurs while the western coal is in transit. The small coal particles burn more rapidly when there is available air; however, when there is insufficient air they tend to plug the grate and fuel bed openings and form dark patches which turn into clinkers.

The older underfeed and overfeed stokers designed for eastern coal will have to have modifications to the undergrate air chamber to allow better control of the air distribution, if western coals are to be used.

Spreader stokers are affected by the same coal properties but to a lesser extent since approximately half of the combustion takes place in suspension. This suspension burning reduces the number of "fines" that reach the grate. However, the fines in the coal tend to burn close to the spreader, sometimes flashing back into the feeder opening. This flash back mode can be dangerous since there is the possibility of a fire in the coal feeder. Coke and slag also have a tendency to build up on the spill plates and rotor blades if the flash back is allowed to persist. This problem can be alleviated somewhat by rotor speed and spill plate adjustments.

The western coal performed well in the spreader stoker units. In some units designed for eastern coal, the maximum attainable load was about 80% while on western coal. This was due to insufficient induced draft fan capacity and as in pulverized units, high superheat steam temperatures. Removing the major part of the moisture from the coal prior to combustion would alleviate both of these problems.

Emissions from Stoker-Fired Units

Sulfur Oxides

The emissions of sulfur oxides from stokers is to a large degree, governed by the sulfur in the fuel. These emissions are independent of load and excess air in the flue gas. Table VI, presented earlier, sets out the results of a SO_x emission comparison for all the coals tested in this study. The overall average SO_x emissions from actual operating industrial type boilers decreases from 1827 ng/J (4.25 lb/MBtu) on eastern coal to 614 ng/J (1.43 lb/MBtu) on western coal, or 66%. This is to be compared to the reduction as calculated from the fuel analysis from 2025 ng/J (4.71 lb/MBtu) on eastern to 710 ng/J (1.65 lb/MBtu) on western coal, or 65%. The sulfur content of the fuel was calculated from analyses of actual fuels burned.

The mineral analyses of the coals tested, given in Table I, show that the western coal contains a high percentage of lime, CaO, and magnesia, MgO. The amount of sulfur trioxide retained in the ash closely approximates the lime content of the ash in all cases. This suggests that the coal may tie up some of the sulfur as a sulfate. The western coal with its greater lime content retains more sulfur than the eastern coal as indicated by the data in Table VI.

Stenhouse, et al., [ref.] have published a study of sulfur oxides emissions from lignite-fired power plants. They found significant amounts of sulfur retained by the ash. By using the following relationship, they could satisfactorily correlate their data.

Sulfur emitted, as % of sulfur in coal =

$$(1.1)\frac{(CaO)}{Al_2O_3} - 10.1\frac{Na_2O}{CaO} + 110.1$$

This correlation could not predict the amount of sulfur emitted in the flue gas as SO_2 when the subbituminous coals used in this study were compared to the actual emissions. The improved correlation gave consistently higher emission factors than actually measured.

Table VI contains the results of fuel sulfur analyses and SO_2 emission analyses for six western and eastern coals. For each coal, the fuel analysis and the SO_2 emissions analysis for the same tests were compared. Where there was more than one test, the results were averaged. The results show that on the average, the western subbituminous coal emitted only 64% of the fuel sulfur available, whereas the eastern base coal emitted 90.4% of the available fuel sulfur under comparable boiler operating conditions.

It can be concluded from this data that naturally reduced sulfur emissions are influenced by coal type and are of a magnitude such that the reductions should be considered when choosing a coal for reasons of SO_x compliance.

Nitric Oxide

Nitric oxide emissions from stokers exhibited a similar dependence on excess O_2 in the flue gas as the pulverized coal firing. At constant load, nitric oxide emissions increased with increasing excess O_2, as well as increasing slightly with increasing load.

However, the slope of the NO vs. O_2 curve is less for stoker-fired units than for the higher intensity combustion devices. Figure 4 shows an interesting NO vs. O_2 result for a water-cooled vibrating stoker. The western coal (Wyoming Bighorn) has a slope of 12 (ppm NO/% O_2) compared to the eastern coal (Kentucky Vogue) which has a slope of 15 (ppm NO/% O_2). Figure 5 gives the NO vs. O_2 plot for the same two coals on an overfed traveling grate stoker without a water-cooled grate. On this unit, both coals exhibit the same NO vs. O_2 dependence. In fact, of the boilers tested, the water-cooled grate was the only unit having different NO vs. O_2 slopes for the two coals tested. It is speculative as to whether the additional cooling of the grate affects the conversion of fuel-bound nitrogen to NO.

Stokers have overall lower NO emissions than pulverized coal units since the stokers operate in a "staged combustion" configuration. The stokers that have little or no suspension burning such as underfed and overfed stokers have a greater degree of staging than do the spreader stokers. In the stokers, the fuel devolatilizes in the fuel bed under reducing conditions; then is mixed with the combustion air above the bed. Mixing is provided by overfire air jets or by front or rear arches in the furnace. Clinkering in the fuel bed establishes a limit to the degree of staging that can be achieved in stokers. Figure 6 shows these limits for a 72.6 MJ/hr (100,000 lb/hr) steam spreader stoker.

Carbon Monoxide and Unburned Hydrocarbons

Carbon monoxide (CO) and unburned hydrocarbons (UHC) emissions from stokers as with all combustion systems, can be controlled by providing adequate excess air and proper mixing to insure complete combustion. High excess air conditions can cause CO and UHC emissions as well as low excess air. Figure 7 gives the results of CO emission measurements on a 45.3 MJ/hr (100,000 lb/hr) steam spreader stoker as a function of excess air for both eastern and western coal. At high load (40.8 MJ/hr (90,000 lb/hr) steam), CO emissions increase with decreasing excess air; however, at low and intermediate loads, a point is reached where increasing excess air results in rapidly increasing CO emissions. This behavior was observed for both coals. At low excess air, CO results from inadequate mixing of fuel and air. At high excess air settings, the fuel bed is thin even to the extent of some uncovered grate area which is thought to lead to local quenching of the flame by the combustion air and incomplete oxidation of CO to CO_2. The western coal can be fired at 2% lower excess O_2 at high load while producing comparable levels of CO emissions. This translates to higher unit efficiency because of lower dry gas and combustible losses.

Table VIII contains unburned hydrocarbon (UHC) emission data for an eastern and a western coal on the same spreader stoker unit described above. Unburned hydrocarbon emissions were higher at low load and high excess air than at high load and normal excess air, thus following the same trends as the CO emissions. No appreciable differences in UHC emissions were noted between eastern and western coals.

Carbon monoxide emissions are a much more sensitive measure of incomplete combustion than are unburned hydrocarbons. A comparison of CO emissions and carbon carryover can be made. Figure 8 is a plot of percent carbon in the outlet flyash of a 73 MW/hr (160,000 lb/hr) steam spreader stoker firing western (Montana) coal. This unit exhibited rather high carbon losses which increased with unit load. The carbon losses on eastern coal were even larger than for the western coal. However, the point to be made here is that by measuring the carbon monoxide emissions, an indication of the other combustible losses can be gained. The CO emissions for the same tests are shown in Figure 9.

Particulate Emissions

Three types of stoker-fired boilers were tested. They were

- spreader stoker
- vibrating grate stoker
- traveling grate stoker

Within the spreader stoker category, four unit sizes and two grate configurations were tested. The stoker at St. Johns was fitted with a dumping grate while the boilers at Madison, Wilmar, and Fairmont were all equipped with traveling grates. The spreader stokers with their greater degree of suspension burning and thin fuel bed have higher particulate emissions than the mass fed vibrating grate and traveling grate stokers. The spreaders are intermediate between the pulverized coal units and the mass fed stokers. Uncontrolled particulate emissions from spreader stokers average about 650 mg/J (1.5 lb/MBtu).

In three of the four spreader stokers, western coal produced markedly lower particulate emissions. In the case of Madison, both eastern and western coal produced the same particulate loadings although the western coal had left more ash. The combustible content of the western coal fly ash was half that of the eastern.

Dramatic reductions in particulate emissions were obtained on both a vibrating grate stoker (65t) and a traveling grate stoker (91t) by switching to western coal. These units both have inherently low particulate emissions because the combustion takes place in thick fuel beds with little or no suspension burning.

For a given ash content in the coal, the quantity of particulate matter in the flue gas from stoker-fired boilers depends primarily upon the amount of burning that takes place in suspension or on the grate. Table VII gives an average flue gas particulate loading from both eastern and western coals as measured before the control devices for the stoker types tested as well as pulverized coal-fired boilers.

Spreader stokers with the greater suspension burning have from two to three times the particulate loading of the traveling grate and the vibrating grate stokers. On the average, the western coal test results showed a bit lower particulate loading than the eastern coal.

In summary it can be concluded that there is a distinct advantage from a particulate emissions standpoint, for switching to western coals.

Boiler Efficiency

Figure 10 presents boiler efficiency data as a function of boiler load at two different coal-fired boilers each burning an eastern bituminous low moisture coal and a western subbituminous high moisture coal. Data are shown for a 67.5 MW(e) (100,000 lb/hr) spreader stoker with a traveling grate and a tangential wall-fired, 108 MW(e)/hr(320,000 lb/hr) pulverized coal unit. The latter boiler was equipped with a tubular air preheater while the stoker was equipped with a feedwater economizer.

An examination of the curves in Figure 10 supports both boiler-to-boiler efficiency differences and the importance of coal properties on the efficiency characteristics of an individual boiler. The efficiency of the pulverized coal boiler is greater than the stoker efficiencies over the load range primarily due to higher excess oxygen and combustible loss characteristics of the stoker boiler. Although dissimilar heat recovery devices are used at each boiler (air preheater versus economizer) this has little impact on the efficiency comparisons since stack temperatures were roughly equivalent at both boilers.

Firing with western coal reduced the efficiency of the pulverized coal boiler by approximately 1% while very similar efficiencies were exhibited by both coals on the stoker unit. In the first case the shift in efficiency

is attributed to the dissimilar moisture content of the two coals which resulted in different "moisture" heat losses. Slight variations in excess O_2 levels, stack temperatures, and combustibles had no appreciable effect on the other heat losses (dry gas loss and solid and gaseous combustible losses).

At the stoker unit, a similar impact on efficiency would be expected if coal properties were the only variable. However, in this case, the combination of higher combustible losses experienced with the eastern coal resulted in similar efficiencies. As a point of interest, the combustible losses were less than 1% for all the pulverized coal tests shown, whereas combustible losses on the stoker unit were 2% to 4% and 7% to 11% for the western and eastern coals respectively. The absence of cinder reinjection and combustion air preheat on the stoker boiler contributed to the rather high combustible losses.

SECTION 5

CONCLUSIONS

This study has shown that western subbituminous coals can be substituted for eastern bituminous coals as an industrial boiler fuel. The western coals are compatible with industrial coal-fired units of current design. Two unit types of older design (underfeed and traveling grate stokers) were found to experience difficulty burning western coal. Some cases have been reported where the maximum load capacity of the boiler had to be limited. This problem can be eliminated by predrying the coal or by increased superheat steam attemperation capacity.

Western subbituminous coals were found to be superior to eastern coals in terms of SO_x, NO_x, particulate, and unburned hydrocarbon emissions. The western coals could be fired at lower excess air and exhibited substantially lower combustible losses than eastern coals.

The size of delivered western coal proved to be a problem in most of the stoker-fired units tested. The coal generally had too large a percentage of fine coal which resulted from the poor weathering characteristics of western coals.

Stoker performance on western coal could be improved if the coal were sized locally at the point of use so that delivery distances could be reduced to about 200 miles.

Boiler efficiencies on western coal were lower due to the high moisture content of the western coal. The reduced efficiency due to the moisture losses were somewhat offset by the lower combustible losses and lower excess O_2 required on western coal combustion.

This study has defined the operational parameters that must be followed in order to successfully burn western coal in industrial-sized stokers and pulverized coal units. Excess O_2 and carbon monoxide monitors for

combustion control would improve overall industrial boiler performance on both eastern or western coal. These controls are necessary since many times the margin of success can be as small as $\pm$ 0.5% excess O_2 in the flue. For the most part, present instrumentation does not provide sufficient precision in combustion control. Operator training and education must go hand-in-hand with improved controls for successful western coal firing.

SECTION 5

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2. Gronhovd, G. H., Tufte, P. H., and Selle, R. J., "Some Studies on Stack Emissions from Lignite-Fired Power Plants," presented at 1973 Lignite Symposium, Grand Forks, ND, May 9-10, 1973.

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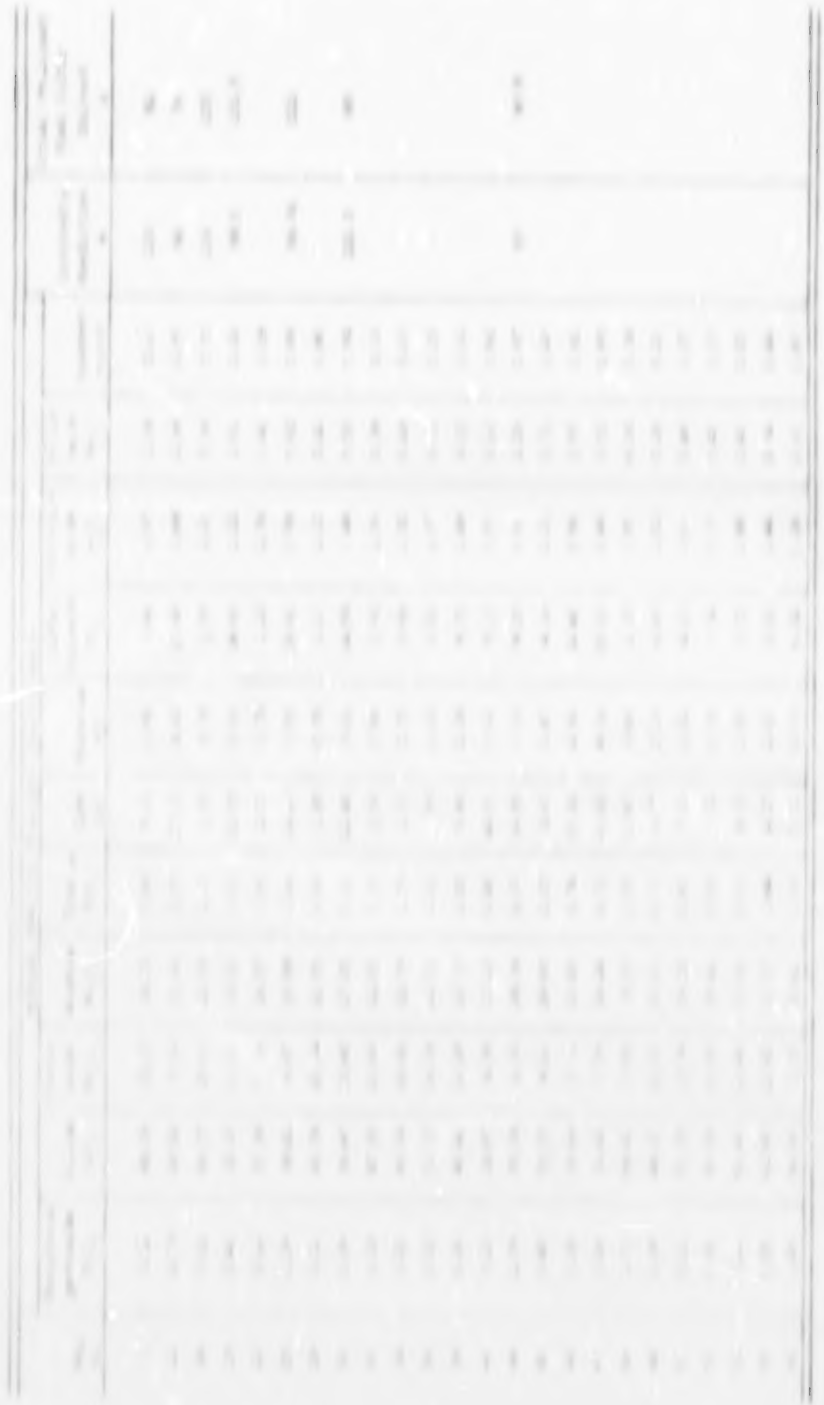

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TABLE II. DESIGN TYPE OF UNITS TESTED AND OVERALL PERFORMANCE ON EASTERN AND WESTERN COALS

TABLE III. SCREEN ANALYSES OF PULVERIZED COAL

Test No:	EASTERN		WESTERN				
	9	16	57	63	71	75	78
Load Ib/hr	56.7	43.6	77.1	59.4	42.6	77.6	43.9
#1b/hr	145	52	170	131	94	160	117
-80 mesh, %	0.65	1.00	5.90	1.40	0.65	8.74	1.51
-80 +100 mesh, %	0.75	1.00	2.30	1.30	2.32	7.70	2.23
-100 +140 mesh, %	2.75	3.35	20.65	4.05	8.31	21.65	6.60
-140 +200 mesh, %	6.95	8.20	14.60	8.70	12.26	16.75	17.46
-200 mesh, %	88.90	86.45	19.55	84.95	55.66	45.15	72.19
Moisture, %	5.15	2.20	22.05	12.75	17.94	19.11	13.75

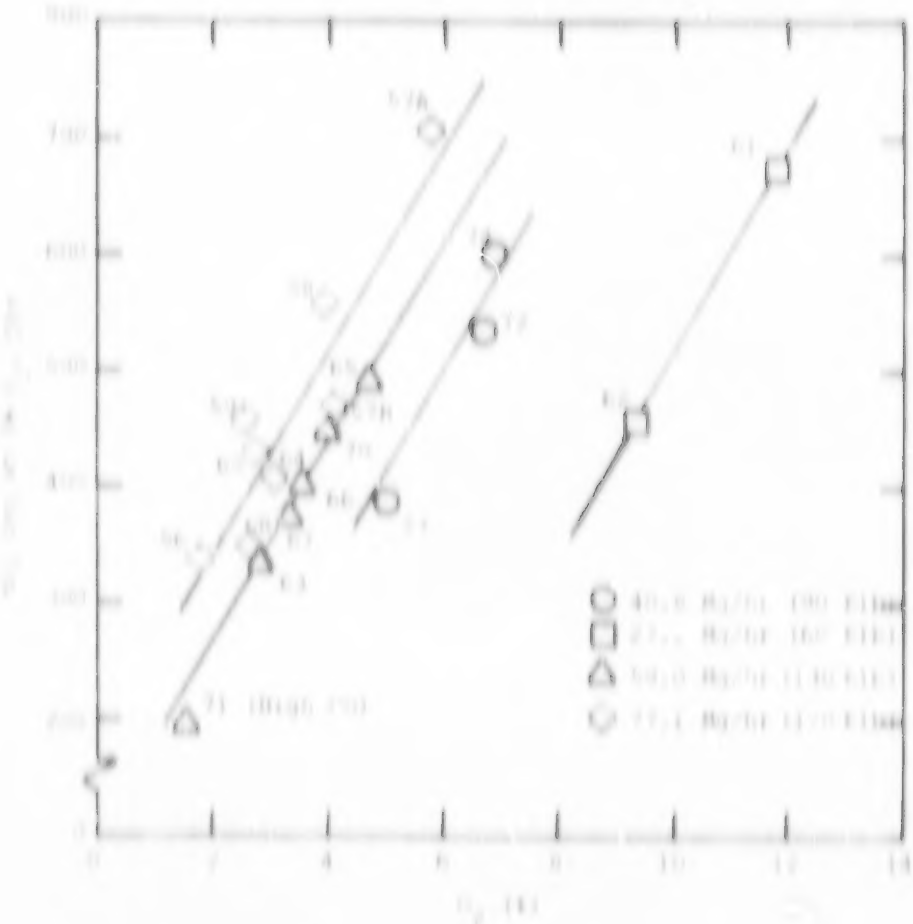
TABLE IV. COAL PERFORMANCE COMPARISON
ALMA UNIT NO. 3

Test No.	Western 66 ESP Inlet	Eastern 9 ESP Inlet
Load, MW/hr (Btu/hr)	59 (130)	59 (130)
Excess O_2, %	1.4	1.4
NO_x at 3% O_2, ppm	598	1283
PM, dry at 3% O_2, ppm	172[a]	490[b]
CO, at 3% O_2, ppm	11	21
Particulate, mg/J (lb/MBtu)	74(0.17)	341(17.987)
ESP Efficiency, %	99.8	99.6
Carbon carryover, % by wt	0.55	4.11
Unburned HC, at 3% O_2, ppm	25	11
Boiler Efficiency, %	87	88.5

[a] 43 mg/J (0.52 lb/MBtu)
[b] 96 mg/J (0.69 lb/MBtu)
Uncontrolled

TABLE VIII. COMPARISON OF HC EMISSIONS
FROM EASTERN AND WESTERN COALS
for 47.4 Mg/ha (100 Ft^3/ft^2) Strip
Spreader Stoker

		Eastern Coal		Western Coal	
Mg/ha	(Ft^3/ft^2)	O_2(%)	HC (ppm)	O_2(%)	HC (ppm)
18	40	15.	114	11.8	125
27	60	12.7	58	11.1	18
41	90	9.3	40	--	--
41	90	8.7	44	8.8	44



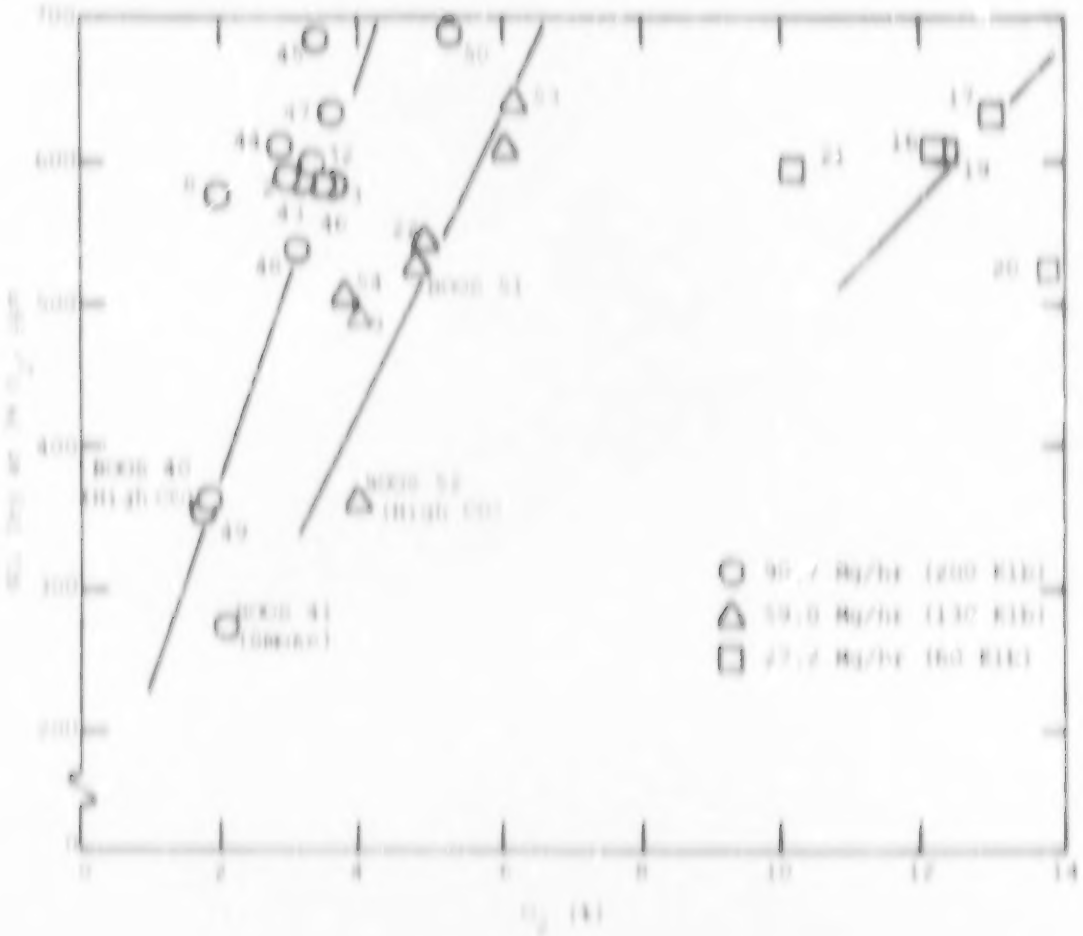


Figure 2: Nitric oxide vs. oxygen - Alma Unit 1; eastern coal; Fuel N = 1.09%

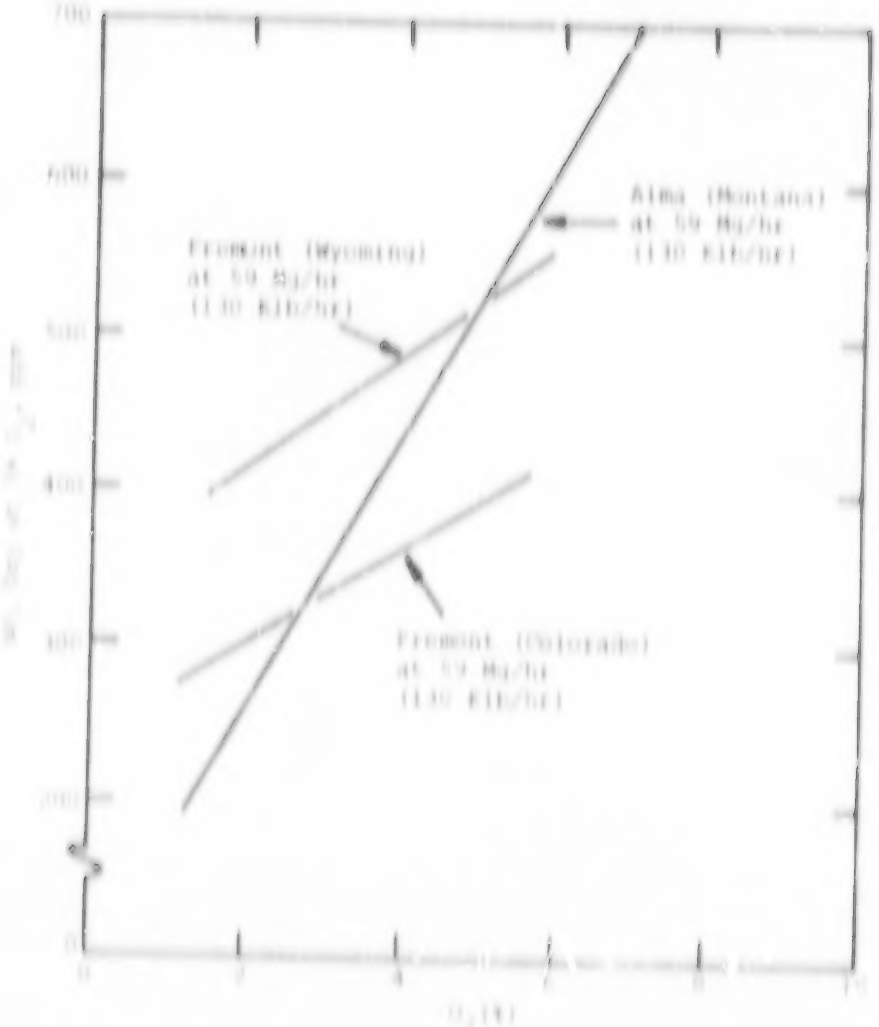


Figure 3. Nitric oxide vs. oxygen - comparison of 104 Mg/hr (230 Klb/hr) front-burner PC boiler and 73 Mg/hr (160 Klb/hr) front-burner PC boiler.

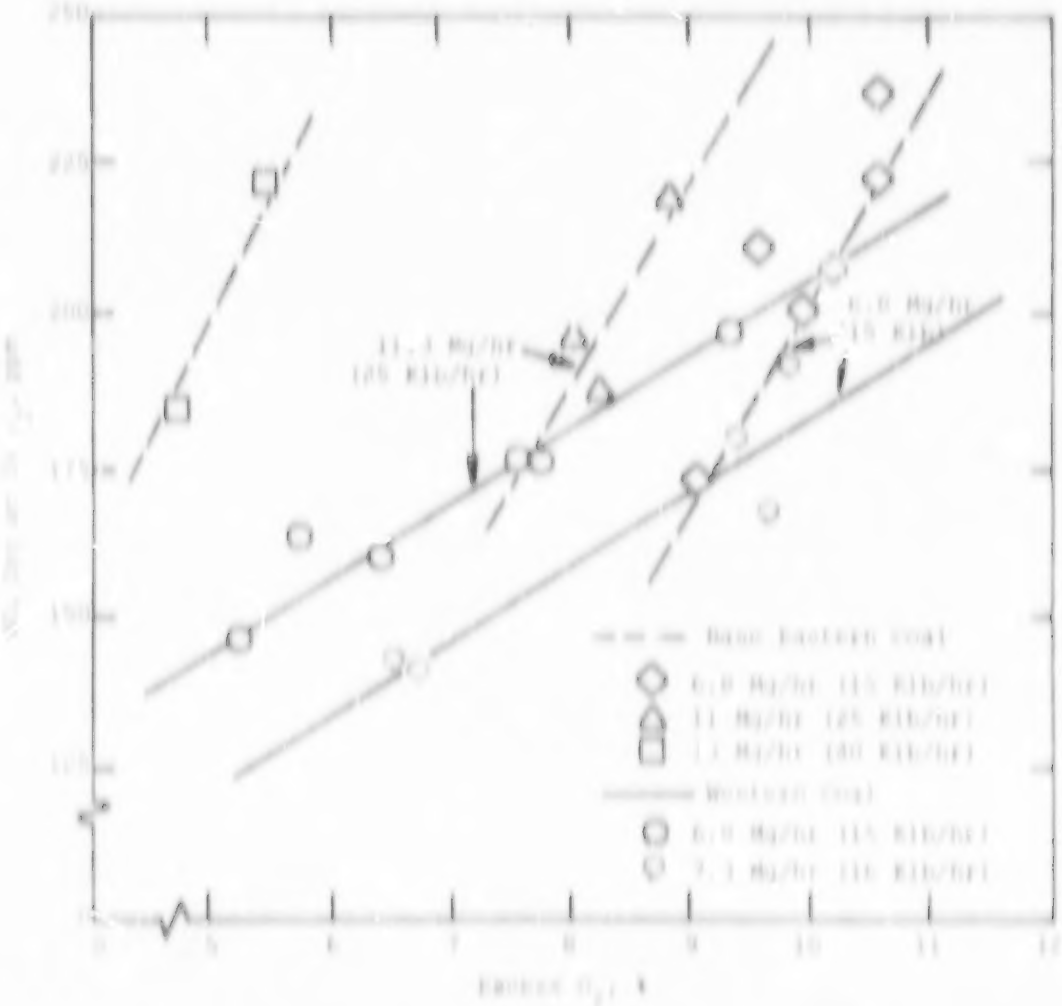


Figure 8. Comparison of western and eastern coal nitric oxide emissions (University of Minnesota/Stoll). Waterwalled vibrograte stoker; 20.8 Mg/hr (45 Klb/hr) steam.

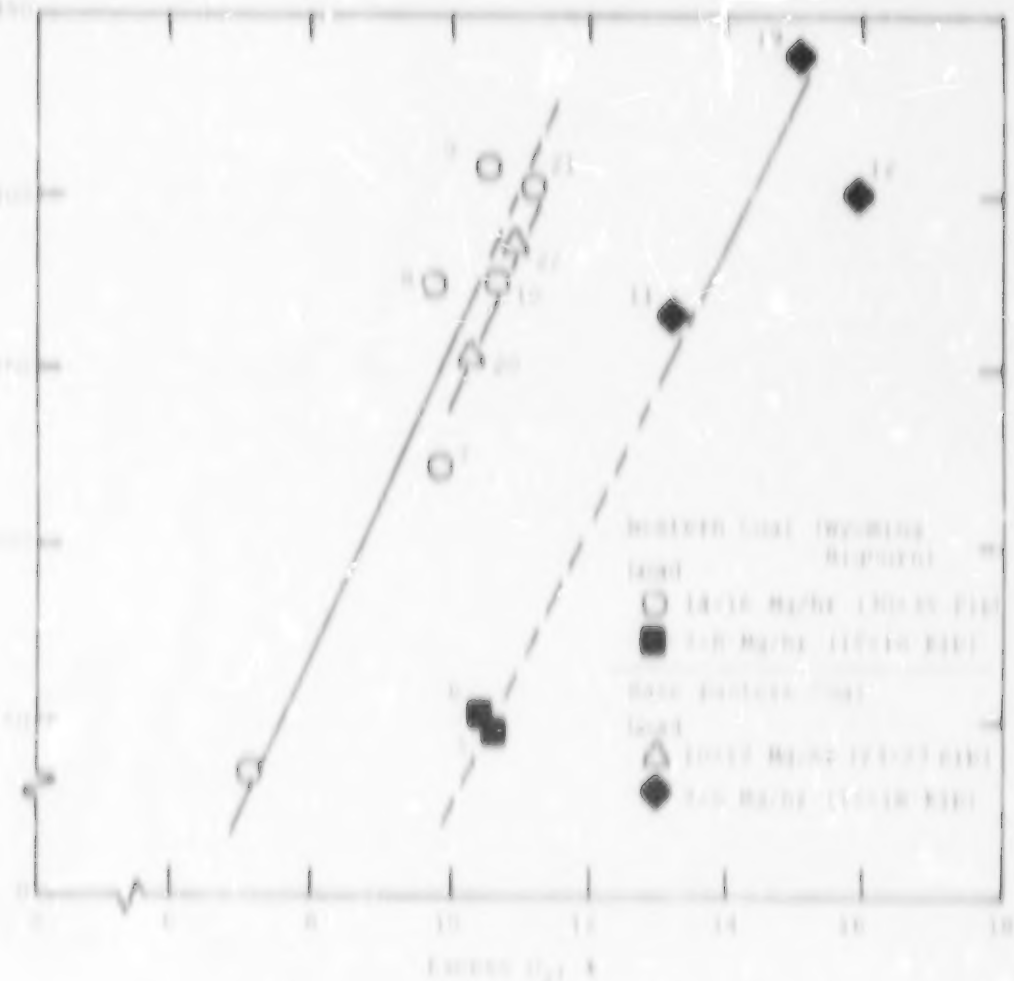


Figure 5. Inviscid travelling wave theory, $M_\infty = 4$ Mach (NO PLOTS) (from University of Minnesota/Duke Center).

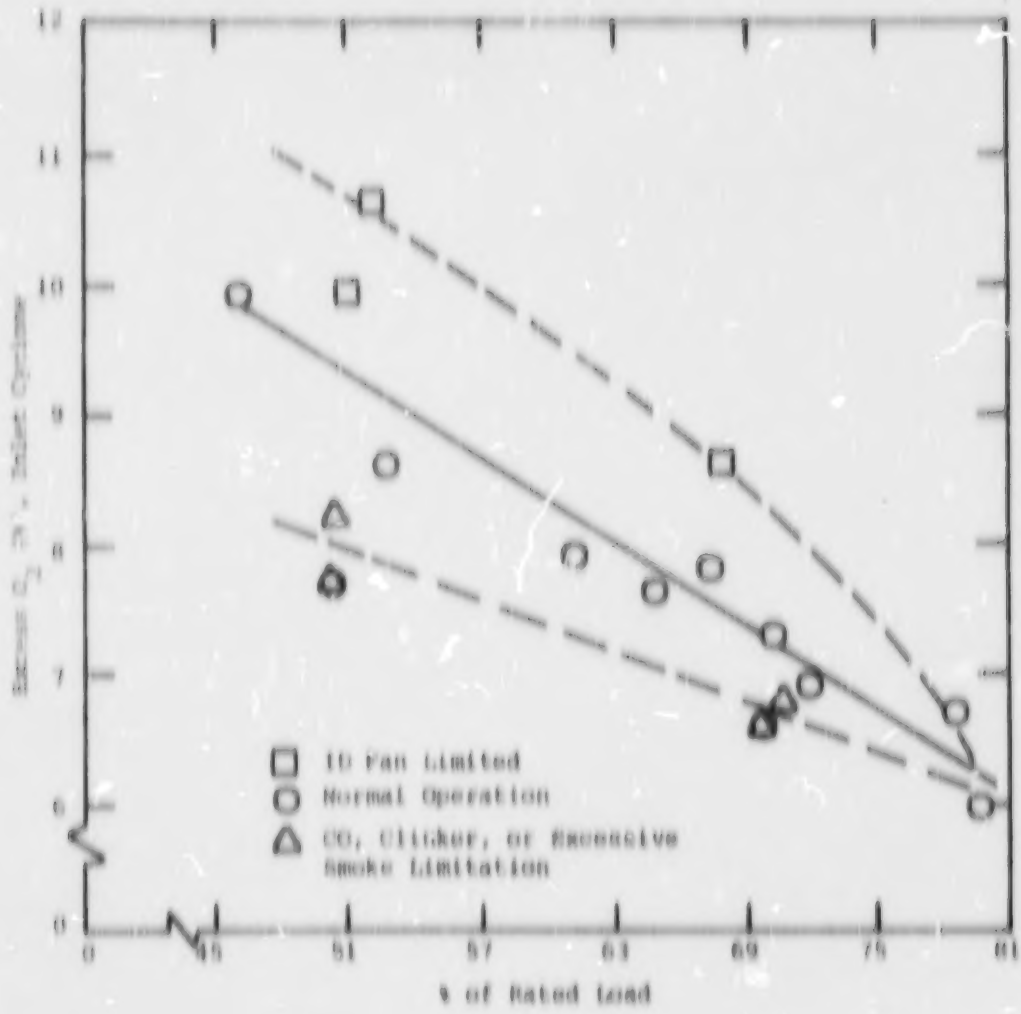


Figure 6. Stoker firing staging limits, 72.6 Mg/hr (160 Mlb/hr) steam, western coal (Wilmar Unit 3).

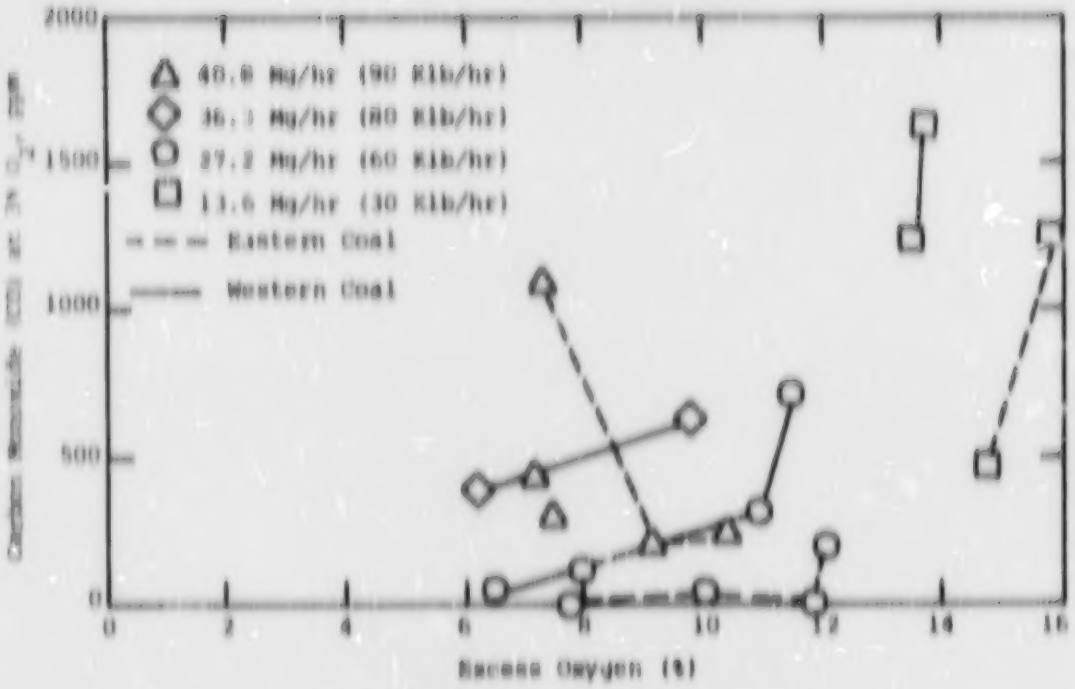


Figure 7. Carbon monoxide as a function of excess oxygen (University of Wisconsin-Madison) - 45 Mg/hr (100 Klb/hr) steam spreader stoker.

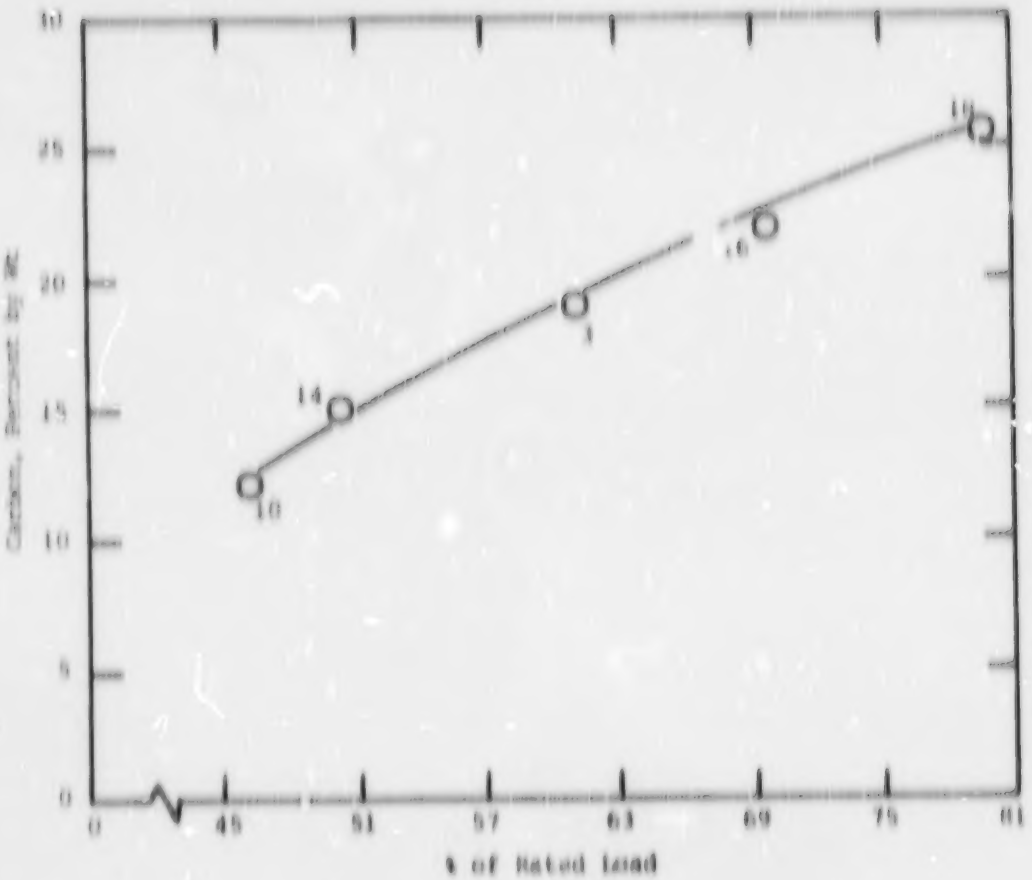


Figure 8. Percent carbon in outlet flyash, 72.6 Mg/hr (160 Klb/hr) steam spreader stoker (Willmar Unit 1), western coal.

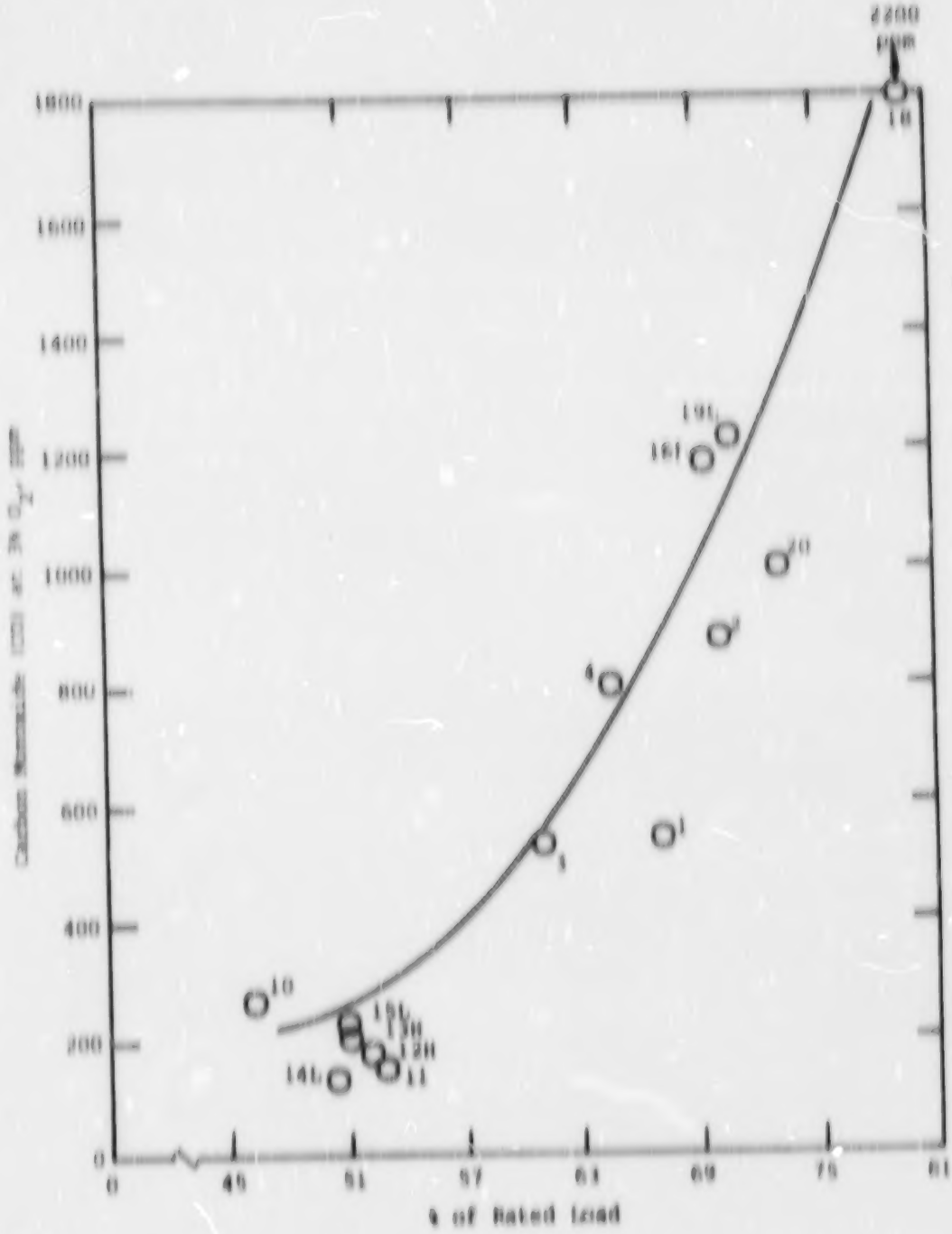


Figure 9. Carbon monoxide emissions versus load (Willmar unit 1, western coal, 72.6 Mg/hr (160 Klb/hr) steam spreader stoker.

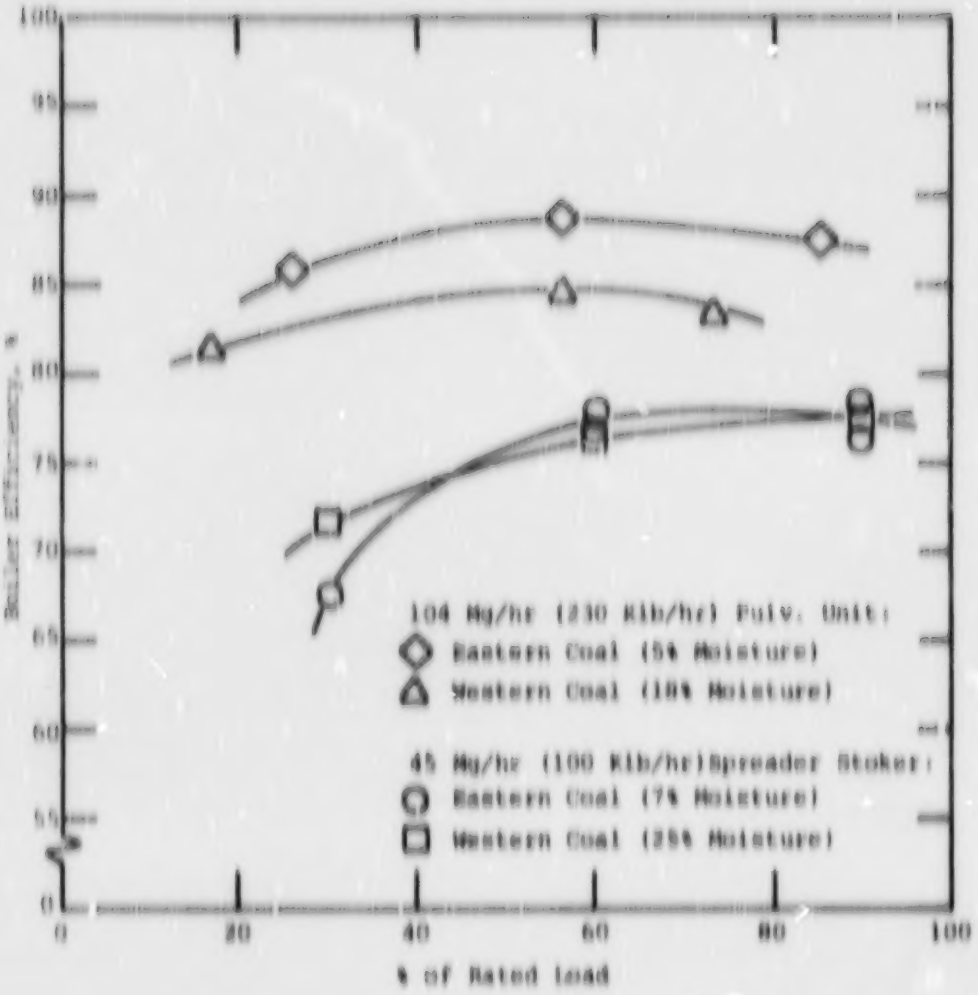


Figure 10. Boiler efficiency comparison of pulverized coal firing to spreader stoker firing for a high and low moisture coal type.

SESSION III:

SPECIAL TOPICS

DAVID G. LACHAPELLE
CHAIRMAN

A SURVEY OF SULFATE, NITRATE, AND ACID AEROSOL EMISSIONS AND THEIR CONTROL

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ABSTRACT

The objective of this anaiytical study was to evaluate the effects of fuel and combustion modifications on the formation of primary acid aerosols and their significance as combustion generated pollutants from large stationary sources. The term acid aerosol is used here in its broadest sense to include all sulfates, nitrates, chlorides, and fluorides in all their forms. Primary acid aerosols are those aerosols which are emitted directly from a source or formed, primarily by condunsation reactants, in the immediate vicinity (0.5 mi); secondary aerosols, formed by reactions downstream in the plume, are not considered. Available field data were collected and interpreted in view of current knowledge of mechanisms of formation of potential acid aerosols and their precursors.

Sulfates, nitrates, chlorides, and fluorides were considered initially; however, based on the data available, only sulfates appear to make a signifi-cant contribution to primary acid aerosols. Thermodynamic calculations bring out significant differences to be expected in the emission of sulfates of minor constituents from coals and oils.

The various combustion modifications for NO_x control, including low excess air, staged combustion, flue gas recirculation, and reburning, are expected to have little effect on emissions of primary acid aerosols. The exception to this conclusion may be firing with low excess air which has the potential to abate both NO_x and acid aerosol emissions. Combustion modifications and fuel changes may lead to an increased formation of small particles which could increase the formation of acid aerosols through various heterogeneous reactions. Most of the effects are rather speculative due to the meager data available. An important technological gap brought out in this study is the lack of information on the specific sulfates being emitted from stationary sources today.

This report was submitted in fulfillment of Contract No. 68-02-1323, Task 49 by Battelle's Columbus Laboratories under the sponsorship of the U.S. Environmental Protection Agency. The work covers the period from February to September, 1976.

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INTRODUCTION

In recent years there has been increasing evidence that sulfates in the atmosphere may be of more concern as a health and environmental hazard than sulfur dioxide. Part of this concern is reflected in the fact that SO_2 levels in the atmosphere have been on the decline, while sulfate levels remain unchanged[1,2]. Historically, it has generally been stated that only about 1 to 3 percent of the sulfur in a fuel is emitted from the combustion system as SO_3 or acid. However, since such acid can lead to various sulfates which might be a part of the particulate emissions, it is important to consider these particulates as well as SO_3 as part of the primary acid aerosol. Further as various combustion modifications (CM) become more widely applied to control NO_x emissions one must be concerned that these previously-held postulations regarding SO_3 and sulfate emissions are valid.

The overall purpose of this study was to survey, compile, and evaluate data on the generation and emission of acid aerosols formed within stationary combustion devices and in particular to determine what effect, if any, CM might have on the formation and emission of primary acid aerosols and what the potential might be for CM to control primary acid aerosol emission.*

Generally it is considered that the acidic sulfates, such as sulfuric acid and ferric sulfate, are of greater concern as health hazards than the neutral or basic sulfates. When speaking of "acid aerosols" in this study, however, the term is used in the broadest sense. Acid aerosols refer here to any and all liquid and solid particles containing sulfates, nitrates, chlorides, and fluorides, as well as sulfates and nitrites of sodium, calcium, ammonia, etc., and all are of equal concern to this study and are included under the term "acid aerosols". The study is concerned not only with total acid aerosol

* EPA Contract No. 68-02-1321 Task 49.

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emission but also their speciation and size distribution. It is important to be so all inclusive in terminology at this time because of limitations to specific relationships between health effects and individual sulfates, nitrates, etc., and because of a current lack of specificity in chemical characterization of particulate emissions.

Although an attempt was made to examine the production and emission of sulfates, nitrates, chlorides, and fluorides in combustion, by far the greatest emphasis was on the sulfates. This came about quite naturally due to the instability of nitrates under combustion temperatures and the dearth of information on chlorides and fluorides in combustion processes. As regards the formation and emission of sulfates as primary aerosols, we have arbitrarily defined as primary aerosol any particulate emitted from the stack and/or produced within the first half-mile in the plume. The need for this definition of primary aerosol is apparent since the chemistry of SO_2 oxidation in plumes is specifically avoided in this study. The slow, secondary oxidation of SO_2 in plumes is covered by numerous other studies[3]. Similarly we have not stressed homogeneous gas phase combustion reactions in this review since they have been summarized well by others [4,5]. The secondary reactions are well documented , and it is important in the context of the present study to recognize at the outset that the emission of primary sulfates, nitrates, etc., is small relative to other pollutants or relative to second generation acid aerosols.

One final comment by way of introduction: throughout this study there was considerable uncertainty in correlating and interpreting such data as was available because of the difficulties in sampling and analyzing for acid aerosol components, especially as regards SO_2, SO_3, and sulfates. This has led to a great deal of uncertainty in much of the data and has made quantitative interpretation extremely difficult. A deep-rooted conclusion that underlies this entire study is that to objectively evaluate the sulfate issue additional work to enhance sampling and analysis capabilities is urgently needed.

ACID AEROSOLS FROM STATIONARY SOURCES

The great majority of emissions which may lead to acid aerosols are sulfur compounds, sulfuric acid, SO_3, and sulfates, although it is recognized that not all sulfates are acidic. Nitrates have not been observed nor are they expected in stack particles, but a small amount of nitrate may be formed in the near plume. The sparse information available on HCl or chlorides is in general agreement with basic thermodynamic considerations that the chlorine in fuel will be emitted primarily as gaseous HCl from the stack. Evidence indicates that total primary sulfates (i.e., those observed within the first half-mile) can be as high as 20 percent of total sulfur emissions or as low as 2 percent.

A significant fraction of the primary sulfates consists of H_2SO_4, based on field measurements. Equilibrium considerations for coal-firing indicate that the remaining sulfates are distributed among $CaSO_4$, V_2O_5, and $ZnSO_4$. Bisulfates are not observed. Specific sulfates are not indentified but field data suggest Na_2SO_4, K_2SO_4 and $FeSO_4$ are also formed. For oil-firing, $NiSO_4$ and Na_2SO_4 are major components of the sulfated fly ash.

The composition and characteristics of particulate matter generated in the combustion process depend on a wide variety of variables including fuel composition, firing method, flame temperature, and amount of oxidant or excess air. Coal and No. 5 and No. 6 fuel oil are the two general types of fuels of most interest in generation of particulate emissions because of their significant ash content and also potential for containing significant amounts of sulfur. They also contain significant bound nitrogen, but nitrates are relatively unstable and it is not surprising that we have uncovered no nitrate particulate information in this study.

Coal Combustion

Most of the mineral matter in coal is made up of kaolinite, calcite, and pyrites. The major elements found in the fly ash are from these minerals and consist of mostly Si, Al, Na, Mg, K, Fe, and Ca. Table I illustrates concentration of the major ash constituents for a variety of coals taken from the general literature and also illustrates some typical measured concentrations

of fly ash sulfur compounds, reported as SO_3, which are of major interest in analyzing the impact of fly ash as a primary acid aerosol.

Generally, the sulfate level (reported as SO_3) is on the order of less than 1 percent up to about 2 percent. Two cases studied by Walker, however, yielding sulfate contents of over 20 percent with the higher case being 24.2 percent [6]. Bolton also recorded an unusually high sulfur content (reported in this case as sulfur instead of SO_3) in one particular coal fly ash sample[7]. It is difficult to say why these high fly ash sulfur contents were observed. They apparently had no relation to coal sulfur content as the two high readings obtained by Walker were on coal of less than 1 percent sulfur while coal used in the Bolton test had a sulfur level of over 5 percent. Also, of all the 11 coal/boiler combinations analyzed by Walker only 3 had over 6 percent sulfate in the fly ash, as SO_3, despite the fact that in all cases coal sulfur content was less than 1 percent. Table II shows variations in the ranges of concentrations of Na, Ca, Mg, K, and Fe in Walker's data for the 3 cases with high sulfate compared to average high and low ranges for 7 cases with low sulfate. Na, Ca, and Mg were consistently higher in the high sulfate cases whereas K and Fe exhibited no clear trend.

Additional data on sulfate content in fly ash is shown in Table III. Three of these cases show sulfate contents for two different locations in the boiler. Where SO_3 was added ahead of the electrostatic precipitator[13] to enhance ESP performance, a clear increase in sulfate content was shown at the ESP outlet. Three out of four readings taken at the air heater and stack show a clear increase in sulfate concentration in the stack[10]. A fifth reading taken with soot blowing illustrates a clear increase in sulfate concentration at the air heater but a low reading in the stack.

In addition to the major ash constituents, fly ash also contains a long list of minor or trace constituents. Certain of these trace elements are of importance in determining the potential for particulates formed in combustion to affect the emission of acidic aerosols. The six elements identified as having the most potential for catalytic effects for converting SO_2 to SO_3 in the flue gas are V, Fe, Ni, Ti, Na, Cr, and Cu. The approximate concentrations

of these elements as reported in 3 different studies are given in Table II. The recent results of both Shotbely[14] and Abel and Rancitelli[15] were related to an NBS/EPA Standard fly ash sample. The results of Bolton were based on results of fly ash samples taken from the Thomas A. Allen Steam Plant[7]. Two numbers are given for the Bolton results indicating measurement by neutron activation analysis (NAA) and by spark source mass spectrometry (SSMS).

The size range of particles resulting from coal combustion is an important factor in estimating their pollutant potential in that it determines the particle surface area available for contact with flue gases, hence affecting adsorption rates with various gas components, and also the relative ease and efficiency with which the particles can be collected.

The results of particle size measurements made at the boiler exit on fly ashes from 69 pulverized coal fired boilers (IGCI/ARMA) indicate that for the most probable distribution the mass median diameter of the particles is about 10 micrometers. This agrees well with data by Walker which indicates that for 30 tests on pulverized coal fired boilers plus 2 cyclone fired units the mass median diameter of the particles was from 5 to 15 micrometers [6].

Stoker fired boilers tend to produce fewer small particles than pulverized or cyclone fired units resulting in an overall larger size distribution. This is due to the lower combustion intensity or heat release rate per unit volume and also to the fact that the coal is burned in larger lumps or pieces. Data on a particular traveling grate stoker fired unit indicates that in 21 tests the mass median diameter ranged from 12.5 to 37 micrometers[16].

Oil Combustion

Particulate emissions from oil fired units result in much the same manner as those from coal combustion. Ash or non-combustible constituents in the oil form particulates both by ashing of refractory components and by condensation of more volatile constituents. Also, there is the possibility of forming condensed carbon particles or soot depending on the combustion conditions and degree of fuel atomization.

Whereas coal ash typically can be at least 5 percent or more by weight of fuel, ash in oil seldom exceeds 0.1 percent. Sulfur contents of oil are also usually lower than those in coal but in the case of residual oil can range up to 5 percent by weight of fuel. Based on analysis of up to 150 samples of residual oil over the 3 year period reported by Orr[17], sulfur ranged from a low of 0.29 to a high of 5.25 percent and ash ranged in content from 0.004 to 1.9 percent (only one-tenth of the samples contained more than 0.1 percent).

Typical ranges of compositions of oil ashes for oils from different regions of the United States and from overseas are shown in Table IV. Also shown is the wide range of concentration of ash constituent in residual fuel oil. Sulfates occur in oil ash in much higher concentrations than in coal ash (values of over 40 percent shown in Table IV). It is noteworthy that oils can contain significant amounts of V and Ni, elements that have been identified as having a potential catalytic effect on oxidising SO_2 to SO_3 thus having a potential effect on sulfate emissions. This differs from coal ash where V and Ni are present in ash at only a few hundred parts per million. Also the nature of vanadium compounds in crude oil is such that they are stable up to 800 F. Hence they are not destroyed by refinery operations and as a result they concentrate in the residuals[18].

Carbon is also seen as a significant constituent in many samples, accounting for over half of the ash content in some cases. According to Novakov carbon could be an important constituent in allowing fly ash particles to adsorb SO_3 from the flue gas forming acid constituents[19].

However, it is important to keep speculation about mechanisms in perspective with regard to the formation of primary acid aerosols. In general, NO_2 and SO_3, precursors to acid, are found to be only several percent of the NO and SO_2 in the combustion system effluent. Sulfate is found, occasionally at high levels, in fly ash and when gaseous and particulate sulfates are combined the total may be of the order of 10 percent[21]. Nitrate is almost never observed. Chlorine in the fuels would be expected to produce some HCl in the effluent but there is almost no data on this point.

However, HCl has been observed[24] and in one case, for a power plant burning pulverized coal, it was determined that virtually all the fuel chlorine appeared as HCl in the flue gas[25] but the fuel chlorine is generally low for most US coals. Thus, based on data presently available to us, to the extent that there is a primary acid aerosol problem, it is a problem of SO_3 and sulfate. The situation may be summarized by considering the results of Cato[26] and Sommer[27] shown in Figure 1. Where the ratio of SO_3 to (SO_2 + SO_3) is shown for a variety of fuels with a range of sulfur contents in a number of different boiler systems. The apparent increase in conversion to SO_3 at low sulfur concentration may be real or it may reflect the uncertainty of current analyses at low concentrations.

Thermodynamic Considerations

Generally the data on particulates does not show the distribution among species that might lead to acidic aerosols. Metals are generally reported as oxides and sulfur as SO_3 or sulfate without identifying the molecular forms. However, equilibrium thermodynamic considerations can be used to provide some insight even though it is recognized that we are not dealing with an equilibrium system. That is, the observed species concentrations are characteristic of the system at equilibrium at a temperature different from that measured. In industrial combustion systems this generally means that the product distribution of pollutants is characteristic of the systems at relatively high temperatures, e.g., at the fire box exit, even though the measurements were made at relatively low temperatures, e.g., in the stack. Thus, the composition is kinetically controlled. This is most striking in the case of SO_2/SO_3 where SO_3 is generally observed to be only a few percent of SO_2 in the flue gas. At high temperatures most of the sulfur would be in the form of SO_2 at equilibrium. But as the equilibrium system cools, SO_3 becomes the predominant gaseous sulfur compound. That the predicted result is not observed means simply that as the temperature drops the rate of SO_2 oxidation slows and the gases pass through the system before they reach equilibrium, i.e., the chemistry is kinetically controlled. This is a gross oversimplification of the many factors involved, of course.

Consideration of the thermodynamic equilibrium chemistry can be instructive since it describes the direction the reactions are moving. Figure 2 is the result of calculations based on combustion of coal of an average composition [38], containing 3.2% sulfur. The formation of both gaseous and condensed species are included in the calculations and they are based on burning with 10% excess air. Calculations were done for lower excess air but are not shown since the results are almost identical. The figure shows the distribution of sulfur among a variety of compounds. The various compounds considered in this analysis are given elsewhere[55]. At high temperatures the sulfur appears almost entirely as SO_2. As the temperature decreases, the system at equilibrium, SO_2 is converted to SO_3 and the two become almost equal at about 800 K (980 F). However, the formation of solid sulfates also increases and as the temperature continues to decrease the solids become the predominant sulfur species and sulfur in the gas phase falls to very low values.

Various gaseous species may contribute to acid aerosol formation, particularly sulfates, and these are indicated in Figure 3, again for the same coal composition with 10% excess combustion air. These are indicative of the expected equilibrium flue gas compositions. It will be noted that sulfur compounds dominate the situation from the standpoint of acid or acid precursors until the temperature drops below about 700 K (801 F). Below this HCl becomes the predominant species because at equilibrium the formation of solid sulfates removes almost all sulfur from the gas stream. That is, at low temperature equilibrium, one would expect most of the sulfur in the system in the solid phase (ash) and most of the chlorine in the gas phase.

In the solid at equilibrium at about 800 K (980 F) the distribution of sulfates, nitrates, chlorides, etc., is dominated by $CaSO_4$. On the basis of mole fraction in the solid the distribution of $SO_4^=$ is

$CaSO_4$	1.4×10^{-1}	$ZnSO_4$	2.6×10^{-3}
$MgSO_4$	1.4×10^{-2}	$PbSO_4$	6.2×10^{-5}
Na_2SO_4	6.9×10^{-3}		

All other sulfates and sulfites are at the level of 10^{-6}, the sum of all such species would be about 2×10^{-5} and include $FeSO_4$, Na_2SO_3, $NaHSO_3$, and $BaSO_4$ in order of decreasing concentration.

A variety of chlorides also would be expected and together they would total about 4×10^{-5} mole fraction with individual compounds in the range of 10^{-6}. It is interesting to note that very little nitrate or nitrite appear as products in these calculations with a total of only about 2×10^{-5} mole fraction.

Fluorides also are present in the same concentration range and the total of various compounds is about 2×10^{-5} mole fraction. Two phosphorous acids also are expected, phosphoric (H_3PO_4) and metaphosphoric (HPO_3), and their total concentration would be about 9×10^{-6} mole fraction.

There was essentially no difference between the 10% and 2% excess combustion air cases calculated for all of these various compounds except some slight general decrease with decreasing excess air, but the change is hardly significant. At still lower temperatures than considered above ($\approx$800 K), there is little change among the species except for $Al_2(SO_4)_3$ which at equilibrium would be the major species. This would occur at the expense of gas phase sulfur (SO_2 and SO_3), but may not happen in practice because the kinetics become too slow. The rest of the species mentioned above are essentially unchanged.

Based on many observations in a wide variety of combustion systems, the composition observed at the stack is more characteristic of equilibrium at higher temperature than the exit temperature. That is, the composition appears to be "frozen" at the higher temperature distribution. If it is assumed that above 1300 K (1800 F) the reaction system is at equilibrium and below it the composition is unchanging, then flue gas compositions can be estimated. On a molar basis for coal with 3.2% S and 10% excess combustion air, the distribution of potential acid aerosol components would be:

SO_2	$\sim$ 2000 ppm	$SO_4^{=}$, H_2SO_4, HF	$\sim$ 0.1 ppm
SO_3	$\sim$ 200 ppm		
HCl	$\sim$ 100 ppm		
NO	$\sim$ 50 ppm		

if the same coal burned with only 2% excess combustion air, then the expected distribution would show an increase in SO_2/SO_3 ratio and a decrease in both NO and NO_2. The expected distribution would be:

SO_2	∿ 2400 ppm	H_2SO_4, HF	∿ 0.3 ppm
SO_3	∿ 70 ppm	NO_2	∿ <0.1 ppm
HCl	∿ 100 ppm		
NO	∿ 10 ppm		

If we made the same assumptions about rates for the solid components and further, that the fly ash would contain about the same distribution of compounds as the total solids, then we would expect in the fly ash, on a molar basis: $CaSO_4$ ∿ 1%; $MgSO_4$ ∿ 0.1%; $ZnSO_4$ ∿ 100 ppm. The various other sulfates, chlorides, etc., mentioned previously would appear at about the ppm level.

In a similar manner, the equilibrium predictions can be compared for fuel oil combustion. Since we are still burning a hydrocarbon fuel, the basic combustion parameters, particularly the temperature range, remain the same. The major difference results from the changed distribution of impurities which can lead to acid aerosols. A distillate fuel will generally have relatively low levels of sulfur, for instance, and very low levels of ash, i.e., the metallic constituents which can lead to a wide variety of inorganic sulfates as in the coal case. A residual oil, on the other hand, will have comparable levels of sulfur, fuel nitrogen, and possibly ash. Therefore the results of equilibrium calculations are similar to those for coal.

Figures 4 and 5 summarize the results for a typical No. 6 fuel oil composition [29,26] and similar calculations were also done for a No. 2 fuel. The products included in the computations are the same as those used in the coal computation except, of course, that those compounds involving elements not included in the fuel are not included in the calculation.

It should be pointed out that chlorine is not included although it is recognized it may be present in some oils. However, the oil analyses available did not include chlorine. The No. 6 oil contained about an order of magnitude more sulfur than the No. 2 fuel and relatively large amounts of vanadium, iron, and aluminum, as well as smaller amounts of a number of other metals. Although calculations were performed for both 10% and 3% excess air, only the 3% cases are shown since the results were nearly the same.

The distribution of potential acid aerosol species in the flue gas is shown in Figures 4 for the No 6 oil. The major difference between the fuel oil cases and that of coal, for equilibrium conditions, is that more of the initial sulfur in the fuel oils remains in the flue gas at low temperature. This results from the lesser ash and hence less formation of solid sulfates. As a result of more sulfur in the flue gas at low temperatures oxidation proceeds further and at the lowest temperature sulfuric acid becomes the major gas phase sulfur species. For the No. 6 oil this could amount to about 0.1 percent of the flue gas at equilibrium, Figure 4. As mentioned previously, however, the system does not come to equilibrium and the calculation represents the potential for sulfuric acid formation, not a prediction of the amount actually formed.

As noted in the coal case, there is little effect due to differences in excess air. From the standpoint of combustion modifications, the maximum difference would be expected from the situation in various types of staged combustion wherein less than stoichiometric air is initially utilized. A summary of effects on potential contributors to acid aerosols is shown in Table V where 3% less than stoichiometric combustion air is compared to 10% excess. It will be seen that at equilibrium at maximum temperature almost all of the sulfur is in the form of SO_2. There is a large increase in SO_3 in all cases when the air is increased but even so the SO_2/SO_3 ratio remains approximately 1000. The main effect in going from less than to more than stoichiometric air is the increase in NO and NO_2. However, the ratio of NO/NO_2 is again about 1000. In staged combustion, additional air is added in some manner to complete combustion at a reduced temperature. For equilibrium

calculations, the results at the reduced temperature and increased air are the same regardless of the distribution of products at the higher temperature so that the calculated combustion system effluent is unaffected by considerations of staged combustion.

The distribution of sulfur in the solid phase at low temperature is what one would expect from the combustion of oil. For residual fuel oils where the total metal content and the number of different metals are both relatively high, the solids will contain a variety of sulfates. For the No. 6 fuel oil used in this example, at low temperature equilibrium, one would find aluminum, iron, magnesium, and nickel sulfates and sodium bisulfate. However, in contrast to the coal case where total ash was much higher, the solids in this example contain only a couple of percent of the total sulfur available in the fuel as shown in Figure 5. Almost all of the sulfur is present as uncondensed sulfuric acid.

Making the same assumptions of frozen compositions below 1300 K (1800 F) as in the coal case, the expected concentration of acid aerosol precursors in the flue gas for the No. 6 oil with 2 percent air and containing 2.8 weight percent sulfur are: SO_2 ≈ 1500 ppm; SO_3 ≈ 100 ppm; NO ≈ 20 ppm. The fly ash would be expected to contain about equal amounts of magnesium, nickel, sodium, and calcium sulfates amounting to a total of a few mole percent.

The No. 2 oil, containing 0.2 weight percent sulfur would be expected to produce in the flue gas, based on the same assumptions: SO_2 ≈ 90 ppm; SO_3 ≈ 4 ppm; NO ≈ 20 ppm. In this case there would be much less fly ash but what there was could contain as much as 10 to 20 mole percent Na_2SO plus Na_2SO_3.

A comparison of equilibrium considerations as they relate to observed SO_3 production in practical boiler systems has been given by Hedley[5] and is shown in Figure 6. The solid lines are theoretical equilibrium calculations for the conversion of SO_2 to SO_3 with either 10% or 0.1% excess air. The dotted line indicates typical actual values at temperatures characteristic of various parts of the boiler system. The horizontal lines indicate expected temperature ranges for various parts of the system. This is consistent with the overall views of mechanisms and kinetics. At high temperatures, point V, the formation of SO_3, is controlled by superequilibrium oxygen atom concentration.

As the gas moves away from the flame and begins to cool the oxygen atoms recombine or react and SO_3 concentration falls toward true equilibrium. When the temperature reaches about 1200 F the kinetics become too slow for SO_3 concentration to follow equilibrium as the gases pass rapidly through the boiler system. Though the concentration of SO_3 may rise somewhat it will not reach true equilibrium.

EFFECT OF FUEL COMPOSITION

That the nature of the fuel obviously will have an effect on acid aerosols and the increased propensity for sulfates with increasing fuel sulfur hardly needs to be stated. However, there are essentially no field data that indicate low concentration of trace species have a major effect on primary acid aerosols. Although there are apparent correlations between sulfates and certain metals in fly ash and deposits, it is difficult to state unequivocally that the sulfate resulted from the presence of the metals.

Based on fundamental data and experiments to show catalytic activity of fly ash constituents, it is to be expected that trace metals will have a large effect on sulfate emissions, but existing data from practical combustion systems do not allow trace metal effects to be quantified.

In the case of coal particulates, the major species are silicon and aluminum oxides which probably are inert. However, Fe, Na, K, and Ca oxides are also generally present in lesser quantities and these have been shown to have some catalytic activity for SO_2 oxidation under at least some conditions. Different metal distributions among coals in conjunction with different combustion modifications probably lead to variations in the distribution and speciation of these metals in the particulate, therefore variation in oxidation of SO_2 is to be expected.

Catalytic Effects of Fly Ash and Deposits

In the temperature range characteristic of the boiler convective heating surfaces, heterogeneous reactions leading to increased oxidation of SO_2 can occur. Several investigations have been made of the catalytic activity of fly ash components in this regard. Fletcher and Gibson [30] showed that for

temperatures above 600 C (1112 F), Fe_2O_3 greatly increased the formation of sodium sulfate from sodium chloride and SO_2, while at temperatures below 600 C, the sulfate was formed only from SO_3 already present. Thus Fe_2O_3 is a strong catalyst in the oxidation of SO_2. These findings were confirmed in the work of Vogel, et al, who found that high relative humidity helped promote this fly ash catalysis[31].

That materials other than Fe_2O_3 in a boiler system can be effective catalysts for the oxidation of SO_2 to SO_3 was demonstrated by Wickert[32]. He found that although Fe_2O_3 was the most active of the materials that he tried, a sample of fly ash brought about a maximum of 36 percent conversion of SO_2 to SO_3 at about 760 C (1400 F). On the other hand, SiO_2 and Al_2O_3 were only weak catalysts in this system. What is most significant, however, was the observation that these catalytic reactions were highly temperature dependent as shown in Figure 7. The catalytic effect of the Fe_2O_3 is greatest at superheater metal temperatures while that of the fly ash goes through a maximum at a slightly higher temperature. The broader peak with Fe_2O_3 indicates the greater importance of this compound as a catalyst for the formation of SO_3, as it operates through a wider temperature range. Obviously the surface area available and length of time for fly ash to spend inside the catalytically active temperature window are of paramount importance in determining the importance of fly ash catalysis.

Manganese dioxide is a powerful converter of SO_2 to sulfate over a wide range of temperatures, from room temperature[33] to at least 340 C (644 F)[31] and so may play a role throughout the entire convection and stack zone of a power plant. High relative humidities (without condensation) are necessary for the catalysis to proceed.

One of the best known catalysts for the conversion of SO_2 to SO_3 is V_2O_5. Residual fuel oils from the Middle East and from Venezuela contain significant amounts of vanadium and in the combustion process this is converted to V_2O_5. As a consequence, there is great potential for SO_3 formation by heterogeneous catalytic reaction with V_2O_5 in the combustion of these oils. Wickert also investigated the effect of V_2O_5 and mixtures containing V_2O_5 and other boiler deposit components on the oxidation of SO_2[34]. His results are shown in Figure 8 in which the temperature dependence of the catalytic reaction is again

apparent. In this case V_2O_5 was a better catalyst for the reaction than Fe_2O_3. A mixture containing 90 percent V_2O_5 and 10 percent H_2SO_4 was just as good a catalyst as the Fe_2O_3. However, the boiler deposit from the burning of residual oil containing vanadium was the best catalyst of all, causing a 90 percent conversion of SO_2 to SO_3. Catalysis by V_2O_5 also was examined by Napier and Stone using short contact times with typical flue gas compositions[35]. The catalyst consisted of V_2O_5 and K_2SO_4 on a silica support. With 1000 ppm SO_2 in the gas stream and the catalyst at 430 C (806 F), from 94 to 98 per[illegible] conversion of the SO_2 to SO_3 was achieved with contact times ranging fro[illegible] 430 milliseconds. When the contact time was held constant at 170 milliseconds, SO_2 conversions ranging from 92 to 98 percent were obtained when the SO_2 content in the gas stream was varied from 340 to 2700 ppm. It was concluded that the required contact time for catalytic oxidation at low SO_2 concentrations is much lower than that used in the contact process for sulfuric acid.

The potential catalytic effect of deposits has been demonstrated further by the work of Glebov, et al[36]. They demonstrated that SO_2 could be oxidised to SO_3 by molecular oxygen in the presence of boiler deposits over the temperature range of 900 to 400 C (1670 to 752 F). The most active catalyst powder was found to be a deposit from the convective bundles of oil-fired boilers. The deposit showed catalytic activity comparable to a vanadium pentoxide powder in the experiments. Maximum conversion occurred at a catalyst temperature of 560 C (1040 F). Further, effective catalysts were prepared from mixtures of V_2O_5 + Fe_2O_3 which had a maximum conversion at 640 C (1184 F).

Using empirical coefficients in conjunction with a simple model of a boiler system, Glebov predicted SO_3 in flue gas as a function of deposit thickness, convective bundle surface area and temperature, and excess air. The predicted values were compared to measured values from a boiler burning a high sulfur oil and good agreement was found. These results indicate that when deposits which may contain vanadium pentoxide are allowed to build up, it is possible that catalysis by the deposits could control the SO_3 effluent. Hence, heterogeneous catalysis by V_2O_5 in flue gases can well be an important source of SO_3. However, V_2O_5 is effective only in a high temperature "window", and

this again poses the question of how combustion conditions affect the available surface area and time that fly ash particles spend in this catalytically effective high temperature window. Furthermore, V_2O_5 is ineffective at room temperatures, and so probably does not contribute to secondary sulfates.

As the simple sulfates remain in the deposits for extended periods of time, they are gradually converted to complex sulfates by the action of the sulfur oxides in the flue gas stream. The formation of alkali-iron trisulfates such as $Na_3Fe(SO_4)_3$ from the reactions of sulfur oxides with Na_2SO_4 and Fe_2O_3 was studied using radioactive tracer techniques by Krause, et al[37] at 600 C (1112 F) and with 2500 ppm SO_2 and 30 ppm SO_3 in a gas stream containin 3 percent O_2. It was demonstrated that the reaction rate of SO_3 to form the trisulfate was 970 times that with SO_2. A similar compound is formed with potassium and in this case the reaction rate of SO_3 exceeded that of SO_2 plus oxygen by a factor of 1260. Experience with trisulfate formation in an operating boiler was reported by Anderson and Diehel, who placed a probe in front of the superheater tubes[38]. Gas temperatures in the region of the probe were 982 to 1094 C (1800 to 2000 F) and the metal surface temperature of the specimens was maintained at 566 C (1050 F). In this case the fly ash collected from the boiler was found to contain 10.3 percent of sulfate expressed as SO_3. The initial deposit collected on the probe after a week's exposure contained 15.7 percent SO_3, and after several weeks time, the SO_3 concentration reached 35 percent.

The significance of the formation of sulfates in deposits and the buildup of high concentrations of sulfates stems from the fact that portions of these deposits are removed periodically from the boiler tubes by soot blowing. This operation is carried out at least once a shift and by its nature creates a large amount of particulate in the boiler in a short period of time. As a consequence the capacity of the electrostatic precipitators is taxed during this period and it is quite likely that a significant portion of particulate sulfate passes through the precipitator and is emitted from the stack. Unfortunately, virtually no data are available yet on these overload conditions which are potential sources of particulate sulfate in the atmosphere.

Catalytic Oxidation of SO_2 by Soot and/or Carbon

The role of carbon as a catalyst to oxidize SO_2 to SO_4 has been reported, primarily by Novakov[19]. He found that freshly generated soot or graphite convert SO_2 to SO_4 which is bound to the particles. Evidence that soot was also catalytically active, especially in the present of water vapor was also found. Futhermore, soot was active at only a specified distance down stream from a flame. This distance may imply the existence of a temperature "window" or limitations of capacity to adsorb and react SO_2. The data shows that the decrease of SO_2 across a sooty filter is independent of SO_2 inlet concentration, a fact which Novakov explains by hypothesizing that the number of active sites on soot particles is controlling rather than inlet species concentrations. Novakov also states that increases in SO_2 oxidation occur at higher O_2/C_3H_8 ratios, although none of these data lie in the fuel lean regime. He attributes this to an increase in the number of "ultrafine, high surface area particles" although it may be due simply to increased O_2 availability. In all his experiments there was a pronounced saturation effect, implying a finite capacity for this process.

However, it cannot be determined from Novakov's work how much conversion is possible through this mechanism. It is not clear whether particle age or temperature is the determining factor for catalytic activity. There is at present no demonstration that this carbon mechanism is not important, and so it seems reasonable to conclude that the mechanism might account for significant primary $SO_4^=$ formation, especially when fresh carbon particles or soot are formed. Clearly further work is required to quantify this effect and to determine its practical significant.

In summary, it is generally found that the sulfate in coal fly ash is less than 2 percent, although occasional higher values are observed, and the sulfur is largely on the surface and present as $SO_4^=$ rather than adsorbed SO_2. Studies of the particulate surfaces suggest the sulfate may be present largely as iron and/or calcium sulfates. Iron is a major constituent of fly ash along with sodium and lesser amounts of calcium. Furthermore, since studies of deposit chemistry have shown that ferric oxide can be an effective catalyst for SO_2 oxidation and sulfate formation, the fragmentary evidence available suggests iron and its eventual distribution and speciation may be an important factor in

the effects of particulates on primary acid aerosol emissions.

Particulates from oil combustion, particularly high ash residuals, are in many respects similar to the e from coal except that they are much more likely to be high in carbonaceous materials and the total amount of particulate will be smaller. The major difference is the presence of vanadium and nickel oxides, which do not generally appear in coal particulates, and are known active catalytic materials for SO_2 oxidation. This occurence correlates with the generally higher sulfate levels found in particulate from oil combustion.

Fuel composition in conjuction with combustion conditions is expected to have a large effect on particle-size distribution. In general, the evidence suggests that the more volatile metals will be concentrated in the smaller particles and maximum flame temperture will effect the amount and species volatilized. These small particles with their relatively large surface area can be particularly effective catalysts for SO_2 oxidation and sulfate formation.

In addition to catalytic effects, differences in size distribution and speciation are also expected to effect the sorptive properties of fly ash and deposits for SO_2 and SO_3 which can effect the eventual formation of sulfates by noncatalytic mechanisms. However, at present it is virtually impossible to quantify these effects.

SPECIFIC EFFECTS OF COMBUSTION MODIFICATION ON ACID AEROSOL

There are very little pilot or field test data which directly demonstrate that a particular combustion modification employed to reduce NO and NO_2 will have an effect, good or bad, on primary acid aerosol. The weight of the evidence is that anything which tends to reduce super-equilibrium oxygen atom concentration in the flame zone will tend to reduce SO_3. On the other hand if the production of particulate, especially very small particles, is increased then the production of acid and sulfate solids might be expected to increase through heterogeneous processes. At this time, conclusions regarding the effect of a particular combustion modification on specific equipment must be highly speculative.

Staged Combustion

There is little experimental information from practical-sized equipment on the effect of staged combustion on SO_3. The pilot scale work of Archer, et al.,[39] investigated two-stage combustion of a high vanadium residual oil with 2.4% sulfur. Their results demonstrated that SO_3 can be reduced essentially to zero when the first stage is slightly fuel rich. They explain their results by noting from previous work that carbonaceous particles inhibit SO_3 formation, react with SO_3, and physically adsorb it. Such changes do not mean SO_3 is completely eliminated from the boiler, however. When air is added at the second stage to complete combustion SO_3 may well be formed, as observed by Hedley[5], in excess of that which would have been formed in single-stage combustion with the same total air. Also, heterogeneous reactions in the boiler section of the system may produce as much SO_3 in spite of staged combustion. This position was summed up by Schwieger [40] "... catalytic oxidation of SO_2 to SO_3 in the superheater and reheater section generally is considered to contribute most of the SO_3. Thus, there might be an unacceptably high level of SO_3 at the air-heater inlet despite an acceptable SO_3 level at the furnace outlet." Pilot scale and more basic studies tend to confirm this expectation; for instance, the previously discussed work of Glebov, et al[36]. However, there is not data from practical systems which substantiate these heterogeneous effects when staged combustion is used.

Flue Gas Recirculation

The situation is quite similar when flue recirculation is used. It is well known that thermal NO and NO_2 are reduced by this CM[41-43], but there is little direct evidence on SO_2 and SO_3. In one investigation Koizumi, et al[44], in studying the combustion of a 2-1/2 percent sulfur heavy fuel oil in a compact combustor (about 10^7 W/m^3), noted that the variable flame length, for the excess air conditions used, decreased as recirculation increased up to 20 percent, then increased slightly up to 40 percent recirculation, before starting a final decrease. Furthermore, the acid dewpoint (measured just beyond the combustor) showed a parallel trend and correlated quite well with

the flame length. The authors ascribe this effect to improved mixing. Whether this acid decrease would be maintained in view of possible heterogeneous reactions in other parts of the system is questionable. However, at this time there is essentially no data regarding SO_3 from practical systems employing this CM.

Low Excess Air

It is well known that low excess air is effective for reducing NO and NO_2[47,48] and limiting acid in boilers. Basic studies indicate that as excess air approaches zero the ratio SO_3/SO_2 also approaches zero. Cosba[49] and Macfarland[50] compute theoretically the values for various mixture ratios, for specific fuel compositions and a range of product temperatures. They demonstrate the expected increase in ratio of SO_3 to SO_2 as the excess air increases. It should be noted that the effect of mixture ratio on the SO_3/SO_2 ratio persists throughout the furnace in their calculations. These results are consistent with "normal" conversion of SO_2 to SO_3 at this point which Gills reported as 0.2 percent to 2.5 percent[51].

Experience with oil-fired systems, where low excess air operation is most practical at the present time, has demonstrated that this mode of operation minimizes the formation of sulfates in deposits in the high temperature portion of the boiler, reduces the amount of sulfuric acid formed, and eliminates the emission of acid smuts. Successful operation with low excess air requires that the oxygen in the flue gas be maintained at levels below 0.2 percent. Such operation requires precise control of the fuel-air ratio in all parts of the combustion system to prevent thermal cracking of hydrocarbons and the emission of smoke. Consequently, low excess air operation has been limited to oil-fired systems, because the technology for burning pulverized coal with such little oxygen does not exist. Normal operation with 12 to 20 percent excess air results in the formation of 25 to 30 ppm SO_3 in the flame with fuels containing 2 to 3 percent sulfur. The excess air must be less than 2 percent to decrease the SO_3 by about half. Further lowering of the excess air results in a rapid drop of the SO_3 level, and at about 0.1 percent oxygen in the flue gas the SO_3 concentration will be reduced essentially to zero.

By redesigning the oil burners and exercising very close control on the fuel-air ratio, Glaubitz in Germany was able to lower excess oxygen to 0.2 percent for routine operations. Under these conditions, the sulfuric acid was reduced to such an extent that the dewpoint approached that of water. Glaubitz stated that after 12,000 hours of operation, the boiler still did not have to be shut down for cleaning, indicating that the strongly bonded deposits which build up as a result of the formation of large amounts of sulfates had not developed in this boiler[52].

Low Air Preheat

Lower air preheat is another change of input conditions which lowers the formation of SO and SO_2. There is considerable information regarding the lower preheat effect on the SO_3/SO_2 ratio. However, as Glasny[36] points out, "data on the influence of flame temperature on process of formation of SO_3 is very inconsistent. It has been firmly established that in pulverized-fuel-fired boilers, the content of SO_3 in the gases decreases --with increasing temperature in the furnace. However, Crumley, et al.[53] on the basis of experimental data they obtained. . ." using kerosene and distillate show an increase in SO_3 to a flame temperature of 1750 C (3182 F) followed by a leveling off. The difference in the results from the two fuels is considerably less than the difference in 2 percent sulfur in the kerosene and 1 percent in the distillate. At 70 percent excess air with kerosene, about 7 percent of the sulfur was in the form of SO_3; at 28 percent excess air, about 5 percent.

Glebov[36], in agreement with Macfarland[50], Gamba[49], and Gudzyuk, et al.[54], shows with thermodynamic calculations that the SO_3/SO_2 ratio decreases with increasing preheat temperature. But Glebov's data on the combustion of high sulfur fuel oil show a constant value of SO_3 from 2100 to 2500 C (3800-4530 F) for two values of excess air. Gudzyuk, et al., indicate possible effects on SO_3 of high excess air regions near cool walls which might explain some of the contradictory results. As discussed previously, SO_3 can be removed from the flue gases by reaction with metal oxides to form solid sulfates, thus reducing the SO_3 concentration in some regions. Or heterogeneous reactions might increase SO_3 under some conditions. Therefore, it is virtually impossible

without additional data to predict what the effect of lower air preheat on SO_3 might be in a given system.

Load Reduction

Based on very meager data, it appears that load reduction has no significant effect on SO_3 emissions. Glebov[36] found no effect of load on SO_3 over a range of 20 percent to 80 percent design load in his study of high sulfur, heavy oil in an experimental furnace. In his theoretical computations he found no change in going from 100 percent to 70 percent load, assuming a catalytic activity of deposits equivalent to that produced by Fe_2O_3, but some increase in SO_3 with decreasing load, assuming catalysis by V_2O_5.

SUMMARY AND CONCLUSIONS

The great majority of emissions which may lead to acid aerosols are sulfur compounds, sulfuric acid, SO_3, and sulfates; although it is recognized that not all sulfates are acidic. Nitrates have not been observed nor are they expected in stack particles, but a small amount of nitrate may be formed in the near plume. The sparse information available on HCl or chlorides is in general agreement with basic thermodynamic considerations that the chlorine in fuel will be emitted primarily as gaseous HCl from the stack. Evidence indicates that total primary sulfates (i.e., those observed within the first half-mile) can be as high as 20 percent of total sulfur emissions or as low as 5 percent.

A significant fraction of the primary sulfates consist of H_2SO_4, based on field measurements. Equilibrium considerations for coal-firing indicate that the remaining sulfates are distributed among $CaSO_4$, $MgSO_4$, and $ZnSO_4$. Bisulfates are not formed. Specific sulfates are not identified but field data suggest Na_2SO_4, K_2SO_4 and $FeSO_4$ are also formed. For oil-firing, $NiSO_4$ and Na_2SO_4 are major components of the sulfated fly ash.

A significant effect of fuel composition on sulfate emissions should be expected. Laboratory and field data indicate that as fuel sulfur level is decreased, the fractional conversion to H_2SO_4 is increased although total

emission decreases. Moreover, based on fundamental data on catalytic activity of various metals, it is expected that there will be large effects on total primary sulfate emissions.

In addition to affecting total $SO_4^=$ formation, fuel composition is expected to have a large effect on emitted particle-size distribution. Volatile metals condense to form very small nuclei, giving a high surface to volume ratio and therefore accelerating catalysis. It should be noted that volatile elements may not always form the most volatile combustion products. Furthermore, small particles may increase the $H_2SO_4/SO_4^=$ ratio, especially if large particles are removed.

Field data to support evidence for V, Ni, etc., catalysis of SO_2 oxidation in fly ash are lacking. There is a scarcity of field data on speciation of sulfate in fly ash, although a correlation exists between the Na, Ca, Fe, and Mg content of fly ash and sulfate content.

Primary acid aerosols are formed by at least two general mechanisms:

(1) High-temperature homogeneous SO_2 oxidation

(2) Dry gas-solid reactions converting SO_2 to $SO_4^=$.

The basic mechanisms of the homogeneous reactions are reasonably well understood and have been extensively reviewed by others[4,5]. However, the effects of heterogeneous reactions are much less clearly defined. Such reactions have the potential to control primary acid aerosol formation but the actual extent of their participation is not certain.

In general, the acid species are not destroyed once formed. Some may be removed from the gas stream by adsorption on particles where they may be in part neutralized and some particles are removed by precipitators, for instance, but such processes are not completely effective. There is positive evidence for the adsorption of sulfur oxides, metal oxides, and chlorides by deposits and subsequent conversion of these compounds to sulfates. Soot blowing removes some such material and probably overloads the precipitator and results in emission of sulfates, vanadates, and other species. Although field data are lacking in this regard, it is probable that such deposits catalyse SO_2 oxidation to some extent but carbon deposits probably do not contribute to the catalysis at deposit temperatures.

Where in the combustion system, and to what extent, primary acid aerosol is formed is highly speculative at the present time. However, the investigators best estimate is:

Flame zone	10 percent of total S converted
Convective pass	10 percent of total S converted
Stack	0 percent of total S converted
Near plume	1 percent of total S converted
Atmosphere	80 percent of total S converted

These estimates of conversion refer to that part of the sulfur in the fuel contributing to aerosol emissions and do not include the sulfur retained in the ash, slag, etc. That is, it is estimated that of the sulfur in the stack effluent, up to 10 percent might be converted to acid aerosol constituents in the combustion zone. Similarly, another 10 percent may have been converted in the convective passes so that up to 20 percent of the sulfur in the effluent may contribute to primary acid aerosol. Probably 80 percent or more of the sulfur emitted in the stack gases will be SO_2, which will be further oxidized in the atmosphere at some later time.

Finally, there is no evidence to indicate that CM (combustion modification) will, in general, be an effective procedure for acid aerosol abatement although low excess air firing, where practical, may be an exception. It might be expected, however, that standard CM techniques for NO_x abatement may adversely affect the quantity, speciation , and particle size of acid aerosol exhaust emissions through increases in the formation of fine particulates and carbonaceous materials.

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TABLE II. [illegible]

Description	Average Concentration Range (percent)					
	Sulfate (SO_3)	Na_2O	CaO	MgO	K_2O	TiO
3 cases high in sulfate	17.6–20.3	0.84–2.02	22.4–23.8	6.0–7.1	0.3–0.49	7.5–8.3
7 cases low in sulfate	1.3–2.6	0.52–0.98	15.2–19.9	2.9–4.4	0.93–1.75	6.78–11.4

TABLE III. [illegible]

Reference	Test Location	Sulfate Concentration in Fly Ash, percent					Comment
Collins, (11)	ESP Inlet	0.2					Measured as sulfur
Jankord, (12)	ESP Inlet ESP Outlet	7.0 5.4					Measured as sulfate
Ogletree, (13)	ESP Inlet ESP Outlet	0.26 0.28	0.46[a] 1.49				Measured as sulfate
Burton, (10)	Air Heater Stack	5.8 7.6	9.3 24.1	8.7 15.8	2.2 1.6	13.7[b] 3.8	Measured as SO_3

(a) With SO_3 injection ahead of ESP.
(b) With soot blowing.

[illegible]

Reference		Constituents, percent												
		SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	TiO_2	P_2O_5	MnO_2	Cl	
[illegible][1], (35)	Raw	62.0	4.0	35.0	11.0	4.7	0.1	1.0	4.0	10.0	0.0	0.0	0.1	Numbers in col. 1 refer
	Burn	5.0	0.0	3.0	1.0	1.0	0	0	0	1.0	0	1.0	0	
[illegible][2], (36)	Raw	30.1	57.0[3]		12.0	4.1	0.4	5.1	4.4	10.0	1.0	0.1	4.0	Numbers in col. 1 refer
	Burn	0.9	0.0		0.7	0.1	0.1	0	0.5	0.1	—	0.0	—	
[illegible][4], (37)	Raw	7.4	5.1	0.3	1.1	2.0	—	10.0	1.2	35.4[5]		40.1	—	Numbers in col. 1 refer
	Burn	10.0	15.0	0.1	4.0	1.7	0.1	1.0	0.0	10.0		34.0	—	
[illegible][6], (38)	Raw	0.0	5.7	7.0	10	1.7	—	7.0	0.5	2.0	1.1	—	—	Ratio per million
	Burn	0	2.0	2	1.0	1.0	—	3.0	1.1	0	0.1	—	—	10 mil.

(a) [illegible] and one California mfr.

(b) Orders from across the United States.

(c) Values from Florida Power Corp. and Tampa Electric Co.

(d) Sandusk. mfr. analysis.

(e) Combined Fe_2O_3 and Al_2O_3.

(f) Combined MgO and K_2O as MgO.

[illegible]

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[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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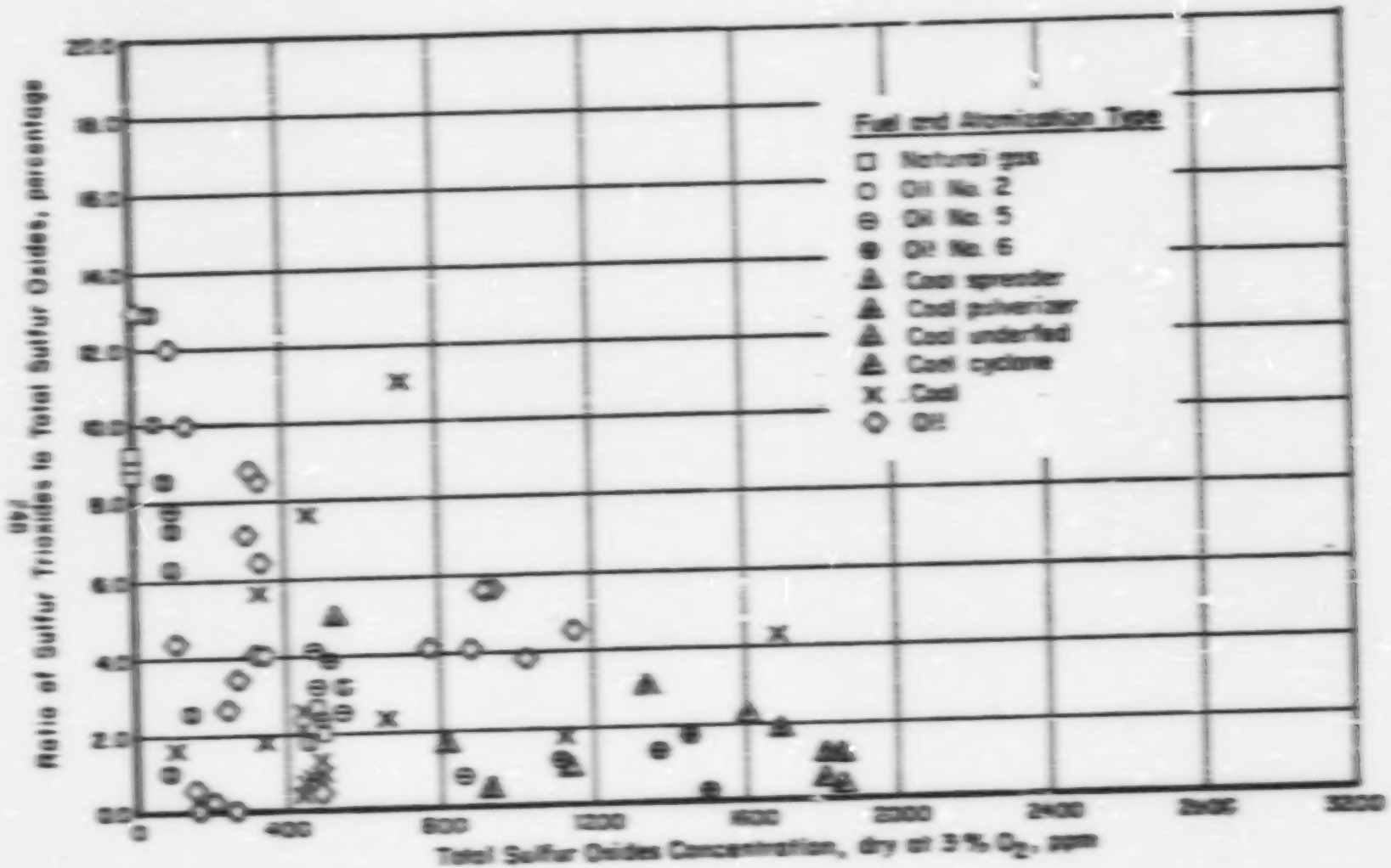

Figure 1. Ratio of sulfur trioxides to total sulfur oxides as a function of total sulfur oxides measured

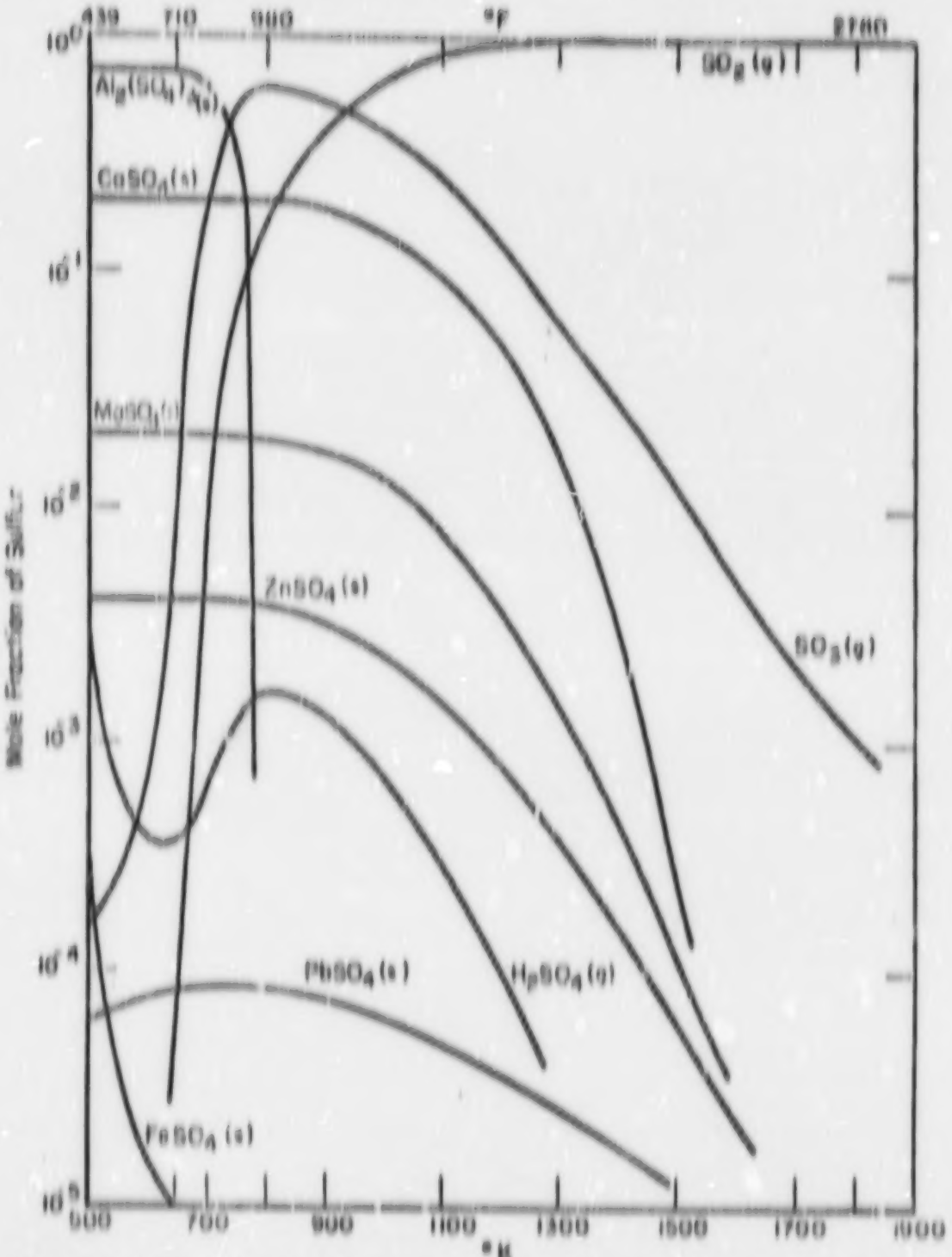

Figure 2. Equilibrium sulfur products for coal combustion with 10 percent excess air, 3.27 percent sulfur

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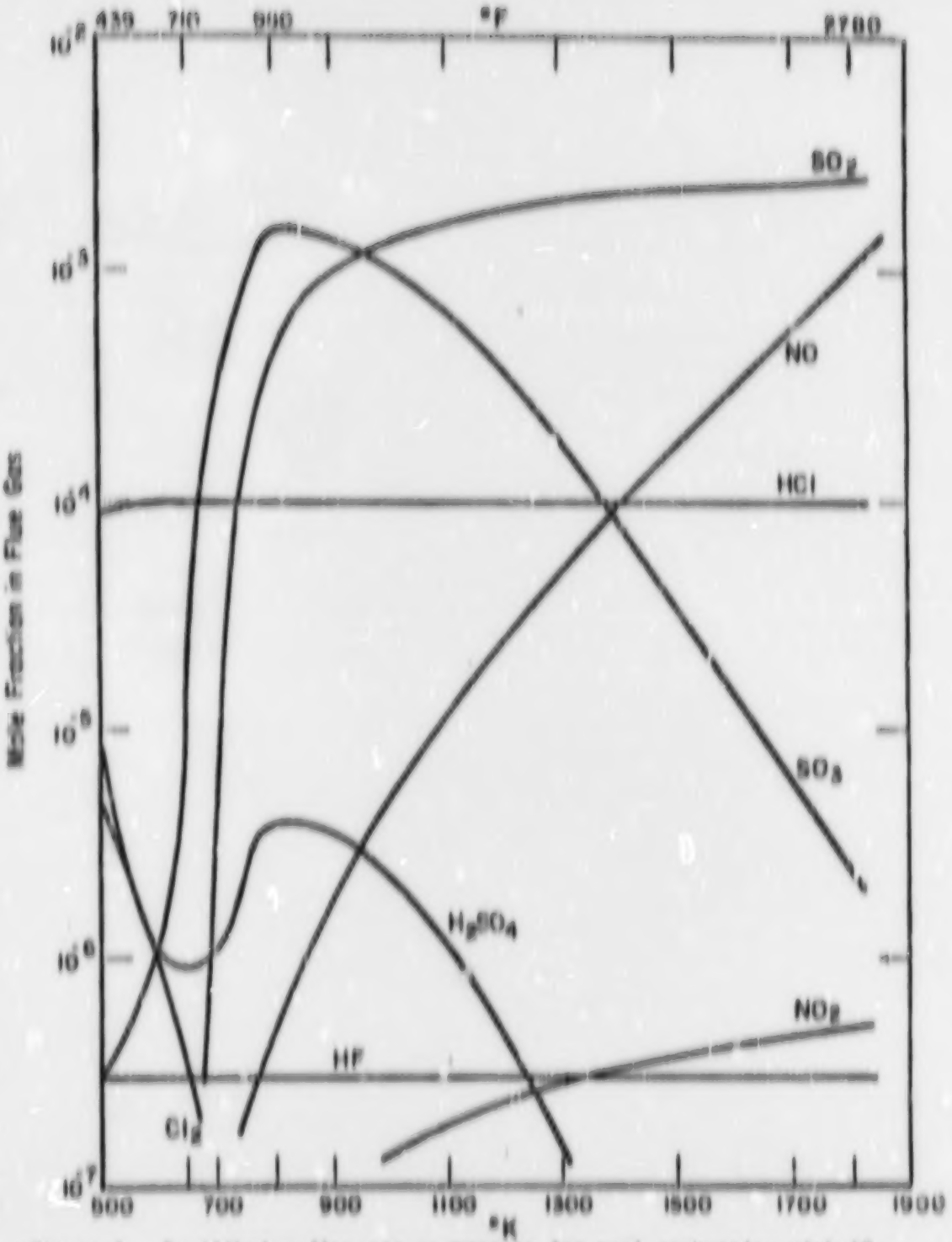

Figure 1. Equilibrium flue gas components for coal combustion with 10 percent excess air, 3.27 percent sulfur

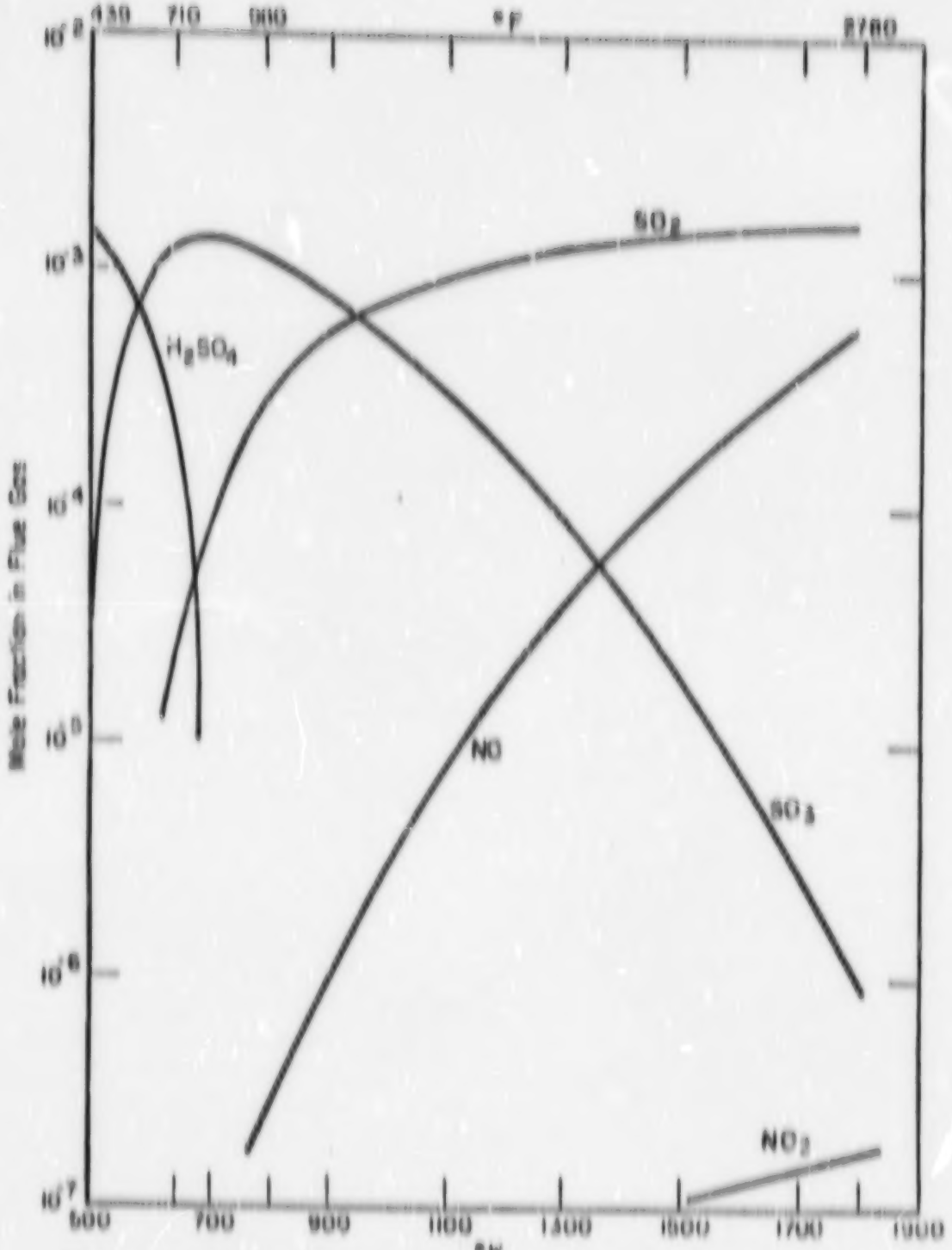

Figure 4. Equilibrium flue gas components for #6 oil combustion with 3 percent excess air, 2.00 percent sulfur

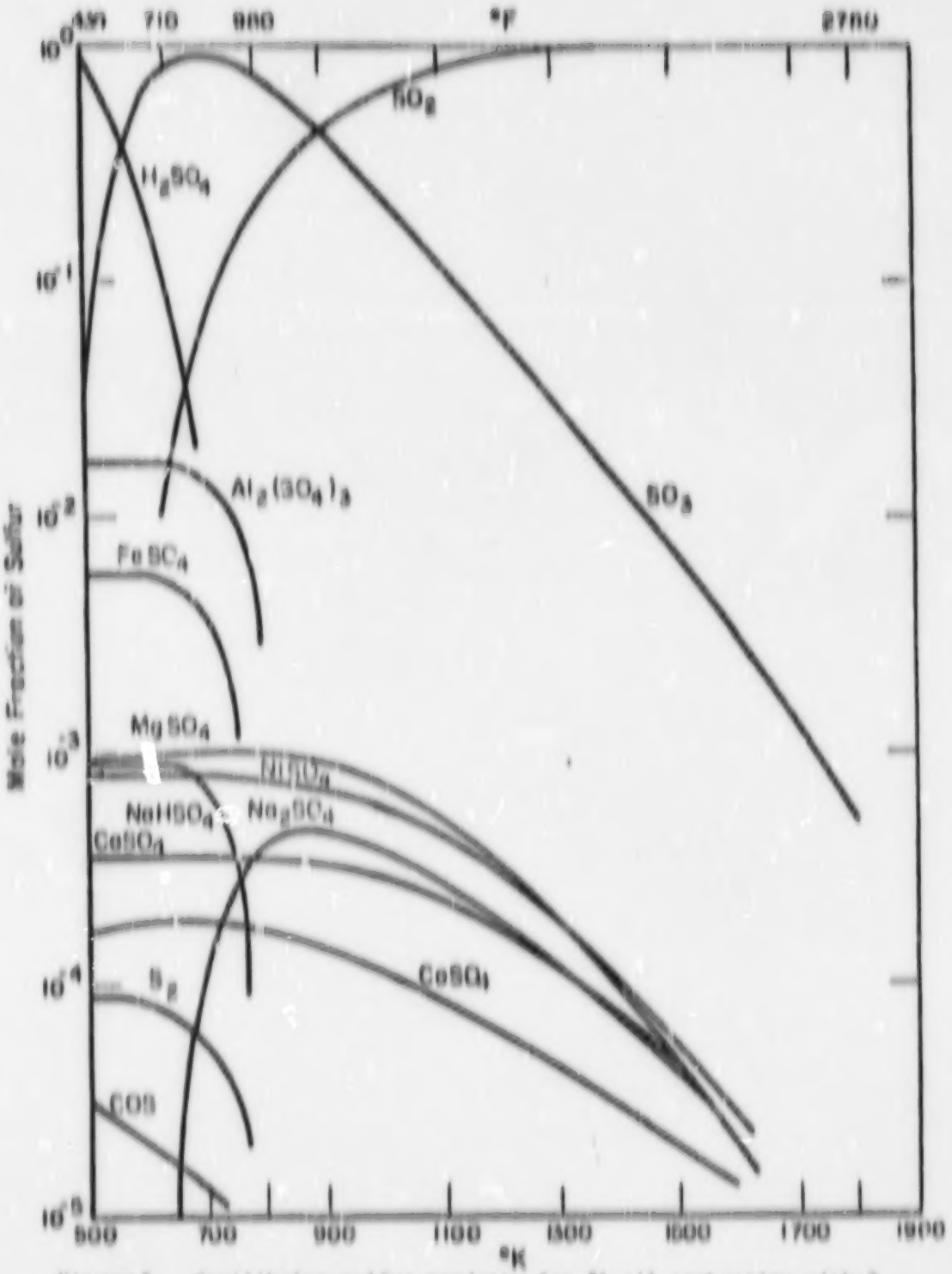

Figure 5. Equilibrium sulfur products for #6 oil combustion with 2 percent excess air, 3.80 percent sulfur

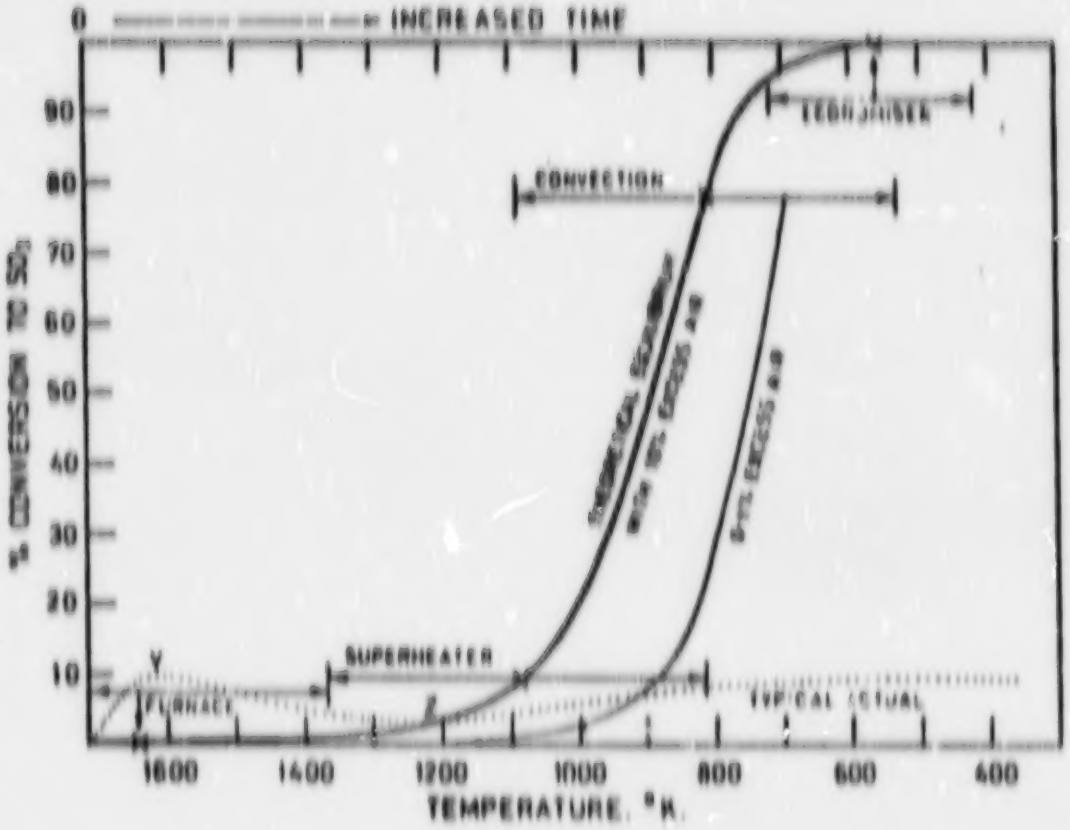

Figure 6. The variation of the theoretical equilibrium yield and possible actual yield of SO_3 with time in a boiler.

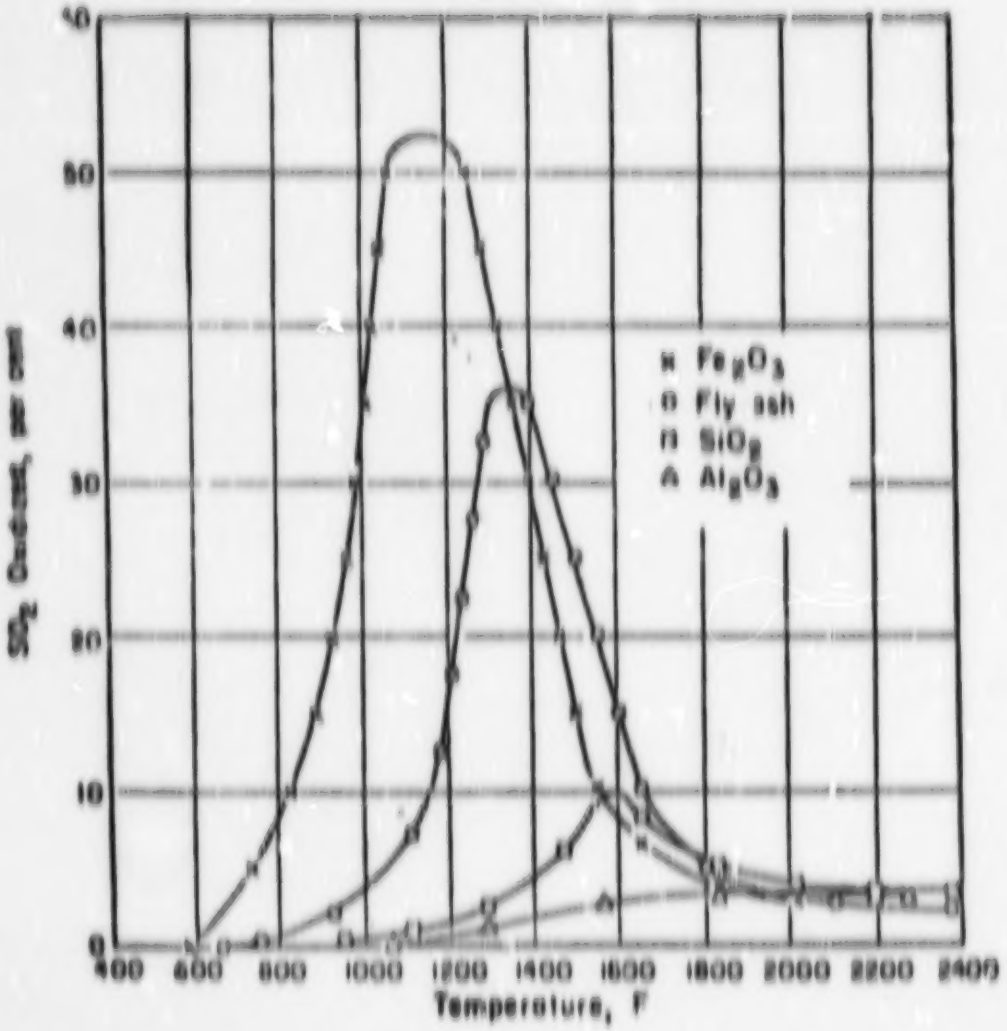

Figure 7. Catalytic oxidation on SO_2 to SO_3 by various materials

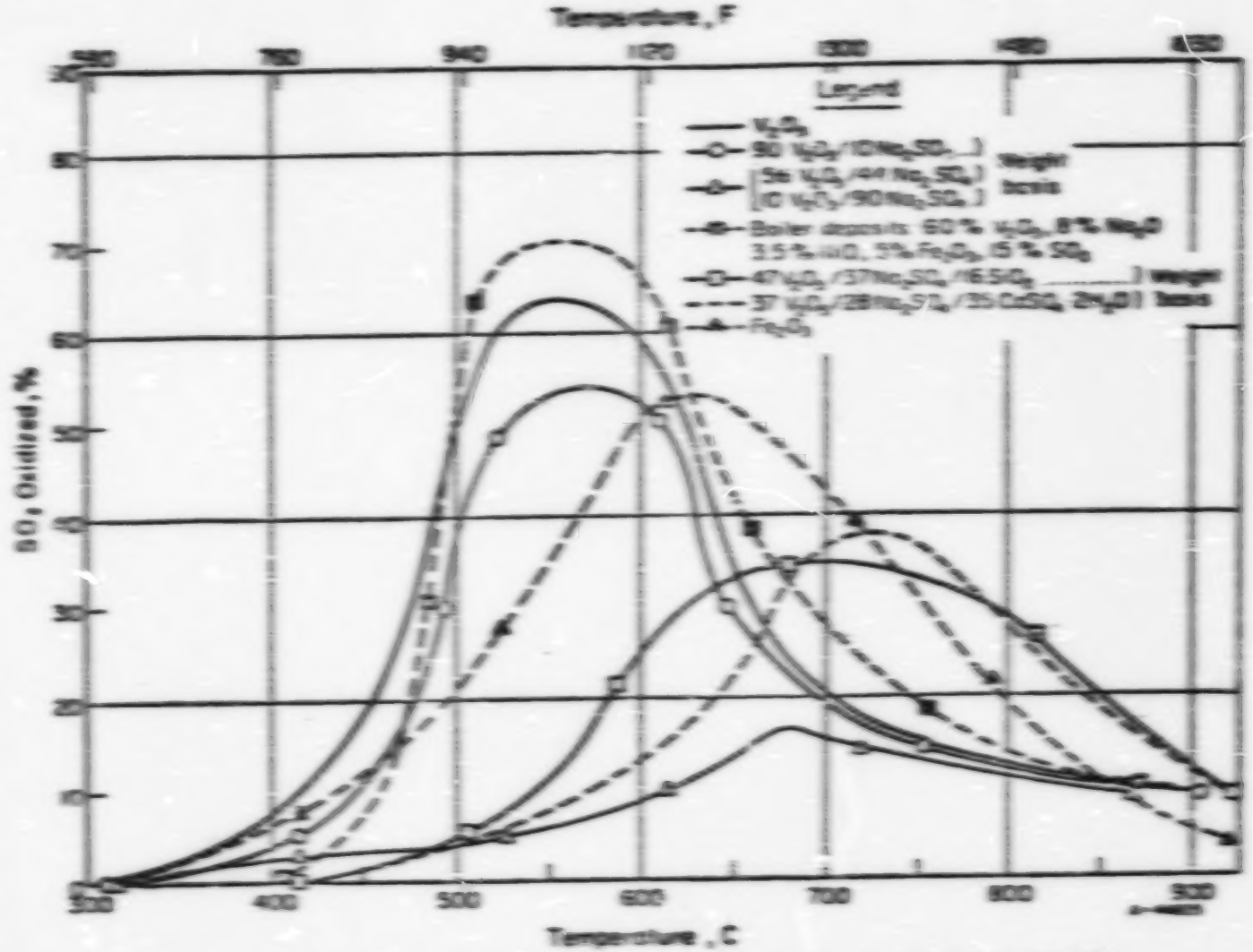

Fig. 7-8. Catalytic oxidation of SO_2 to SO_3 by various materials

INVENTORY OF ATMOSPHERIC EMISSIONS FROM STATIONARY POINT SOURCES

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ABSTRACT

This paper describes the first and second years of a stationary source combustion-related atmospheric emissions inventory being conducted by The Aerospace Corporation for the EPA. This is a 3-year study aimed at assisting in the establishment of priorities for detailed studies of techniques for the control of combustion-related emissions from stationary sources. The inventory includes emissions of oxides of nitrogen, unburned hydrocarbons, carbon monoxide, and particulate matter, not only from recognized major stationary combustion sources, but also from other stationary source categories in which combustion plays a secondary role. During the first year of the study, emissions were established for 1975 and estimated for 1980 from boilers, internal combustion engines, chemical manufacturing, and petroleum refining. During the second year, emissions were calculated for 1976 and 1981 for primary metals and hydrocarbon evaporation, as well as for the four industries studied the first year. This paper identifies approximately 85 percent of particulate matter and 93 to 97 percent of nitrogen oxide, hydrocarbon, and carbon monoxide emissions from stationary point sources. The third year of the study will raise the inventoried emissions to greater than 90 percent for all four pollutants. The emission rates were calculated based on process usage rates, emission factors, and time rate of change of these variables for the respective categories of stationary source of emissions. The usage rates and their slopes were obtained from agencies such as the U. S. Department of Commerce and the EPA National Emissions Data System. The Emission Factor values and slopes were based on data extracted from various reports reflecting either empirically or theoretically derived emissions.

In addition to estimating the annual nationwide emission rates of the four referenced pollutants, the uncertainty of those rates was established. Statistical engineering estimates, current and potential legislative environmental controls, and several independent sources of data were considered in calculating these uncertainties.

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SECTION I

INTRODUCTION

For several years Aerospace has been studying control of combustion-related air pollution from stationary point sources, specifically those of oxides of nitrogen (NO_x), hydrocarbons (HC), carbon monoxides (CO), and particulates. Since current methods of control of oxides of sulfur (SO_x) are not combustion-related, air pollution by SO_x was not studied. In order to put combustion-related air pollution in its proper perspective, it was also necessary to study the major non-combustion point sources of the four air pollutants. A point source of air pollution is defined by the National Emissions Data System (NEDS) as a single point of discharge of more than 100 tons of a given air pollutant per year. The aggregate of large numbers of air pollution sources which are too small to qualify as point sources are called area sources. Although area sources were specifically ruled out of this study, in some cases the possible nationwide pollution contributed by certain area sources was very large compared with the point sources. Some effort was made, in such cases, to at least point out this potential.

The basic source of data, and the model for the data cataloging and reference system was the NEDS. The NEDS system, on the average, tends to represent data from the 1970 to 1974 period and does not provide a means of updating or projecting into the future. The NEDS, however, does represent the largest single nationwide emissions data base available. In order to provide data on which decisions can be based regarding allocation of resources for research in control of combustion-related air pollution, it was considered necessary that the emissions be projected at least 5 years into the future, and that some estimate be made of the uncertainty of the resulting projections. As a result, the NEDS data were used as one source of relatively current data, particularly for the distribution of emissions between various detailed sources within an industry, but other surveys and analyses were studied as well to develop means of predicting changes in the fuel or process usage rates and emission factors in the near future.

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The primary data stored in the Aerospace computer data base are: (a) the best estimates of current annual charge rates and emissions factors; and (b) the probable linear slopes, or changes with time, of these two parameters into the near future. Engineering estimates of the range of uncertainties in the charge rates, emission factors, and the slopes of each are also included. The computer program, then, can project usage rates and emission factors to any date in the future, along with the uncertainties in those projections. Total nationwide emissions at those future dates are calculated from the product of the projected charge rates and the projected emission factors. Because of the uncertainties in the slopes, of course, the uncertainties in emissions projected far into the future become so large that the projection becomes useless. Figure 1 shows an example of projection of the best estimates and uncertainties of the annual charge rate and the emission factor and the resulting projected emissions of, in this example, NO_x.

The first year of this study included the categories of industrial and utility steam boilers, stationary internal combustion engines, chemical manufacturing, and petroleum refining(1). The second year added the categories of primary metals and evaporation (2). The third year, nearly complete, adds mineral products, secondary metals, and wood products, as well as including a short study to update the rapidly changing category of steam boilers (3). These nine categories of air pollution sources are divided into more than 400 sub-categories, in five levels of primary and summary data. Each primary data sub-category requires 40 separate data entries to describe charge rates, emission factors, slopes, and uncertainties for the four air pollutants.

Table I shows the scope of the inventory. All data in Table I except the distribution of the four air pollutants among the stationary point source categories were obtained from a summary of NEDS data run in 1976. Although the NEDS data contain updated emission factors, they are based on process usage rates of the 1970 to 1974 period. The distribution of emissions between the stationary point and area sources and the mobile sources, therefore, generally reflects that time period. These data are shown here only to orient the scope of the subject inventory with respect to all other sources. This inventory, then, restricted to stationary point sources, addressed the emissions from (approximately) as little as 30 to as much as 90 percent of all of the artificial sources of the four air pollutants.

SECTION 3

RESULTS

The data shown in Table II for the category of stationary point sources were developed in this inventory for the year 1976. Data are shown both for the total of all stationary point sources and for those sources which are combustion-related. Within the category of stationary point sources, steam boilers (utility and industrial) clearly dominate the total of NO_x and particulates emissions. This is not necessarily because these sources are particularly dirty but because the magnitudes of the fuel usage rates are so high. This category includes the generation of electricity and all other industrial process uses of steam but excludes steam heating of commercial and residential buildings.

Similarly, evaporation of petroleum products, surface coatings, and cleaning solvents (non-combustion sources) dominates the emission of hydrocarbons from stationary point sources. Major emissions of carbon monoxide are shared primarily by the petroleum and the primary metals industries.

Table II also shows that, perhaps as expected, NO_x and CO emissions nearly all result from combustion. About half of the particulate emissions result from combustion, largely from coal combustion in steam boilers. Since the combustion processes, to be efficient, should oxidize all of the hydrocarbons in the fuels, little of the HC emissions results from combustion.

Figure 2 shows the trends in the emissions of the four air pollutants over the period 1976 to 1981, as projected in this inventory. All are shown to be decreasing, nominally from as little as 13 to as much as 34 percent. Figure 2 also shows the estimated ranges of uncertainty in the data and projections.

Table III shows a more detailed breakdown of the major stationary combustion-related sources of NO_x and particulate emissions (i.e., steam boilers). NO_x from stationary point sources is clearly dominated by utility and industrial boiler combustion.

Bituminous coal combustion currently contributes about three-quarters of the NO_x from steam boilers, both because nearly two-thirds of the heat input to steam boilers comes from bituminous coal combustion and because the EPA NO_x regulation for coal-fired utility boilers is 2 to 3 times those for oil- or natural gas-fired boilers (0.7 versus 0.3 and 0.2 lb of NO_x per 10^6 Btu heat input for coal, oil, and gas, respectively). By 1981 bituminous coal is expected to contribute more than 92 percent of the NO_x emissions from steam boilers and nearly three-quarters of the NO_x from all stationary point sources.

Table III also shows that nearly half of all of the particulate emissions from stationary point sources currently result from steam boilers and 94 percent of this results from bituminous coal combustion in these boilers. The small increases in some of the particulate source percentages are largely due to a small decrease in the total of particulate emissions from all stationary sources over that time period.

Figure 3 shows a further breakdown of the NO_x emissions from utility boilers firing bituminous coal projected for the year 1981. As expected, conventional pulverized coal boilers dominate the NO_x emissions, but, perhaps unexpectedly, NO_x emissions from cyclone-type boilers remain high. This is largely because the NO_x emission factor for a cyclone furnace is more than twice that of the average for bituminous coal-fired utility boilers. Thus, although approximately a 30 percent improvement in the emission factor is projected and fuel usage in cyclone furnaces is expected to remain low (14 percent of total bituminous coal combustion in utility boilers), the NO_x emissions from this type of boiler are expected to remain significant.

The next largest sub-category of NO_x emissions from bituminous coal-fired utility boilers is the tangential configuration. This results from the large fraction of this coal which is burned in utility boilers of this configuration (39 percent of the bituminous coal) rather than from a high emission factor (83 percent of the average).

Figure 4 shows a similar breakdown of particulate emissions projected for 1981 from the predominant combustion sources, utility boilers burning bituminous coal. Again, conventional pulverized coal-fired boilers represent the largest fraction of particulate emissions from this source category (91 percent). Particulate emission factors, however, are much more a function of the control equipment used on the coal-fired boilers than of the firing type. As a result, the fractions of the total particulate emissions represented

by each sub-category tend to represent the fraction of coal burned in boilers of each of the firing types.

The major contributions to carbon monoxide (CO) emissions from combustion-related sources are shown in Figure 5. More than half of this CO results from processes involved in the catalytic cracking of petroleum during the refining process. The related combustion process is the periodic regeneration of the catalyst by burning off the coke (with air) which becomes deposited on the catalyst. There is a great deal of uncertainty in both the current and projected levels of CO emissions from this source (±38 percent in 1976 levels and ±68 percent in 1981 levels). This results largely from the great disparity in current emission factors obtained from various sources and from the lack of data from which to project the rate at which refineries will be modernized in the future and brought into compliance with new standards of performance. The best estimate of this inventory for CO emissions from petroleum refineries for the year 1976 was higher than those reported in the NEDS summary by more than a factor of five. This discrepancy, and the large uncertainties, have not been adequately resolved.

The CO emissions from blast furnace and basic oxygen furnace operations, shown in Figure 5, are included as combustion-related sources simply because they represent the high temperature oxidation of carbon. Carbon black manufacture involves fuel-rich combustion of natural gas and oil, to form the carbon black. As a result, the off-gases are rich in unburned hydrocarbons and CO. While a great deal of effort is made, primarily for reasons of process efficiency, to capture the hydrocarbons, CO emissions are essentially uncontrolled.

Figure 6 shows a breakdown of the major stationary point sources of total hydrocarbon emissions. The figure shows that nearly two-thirds of these emissions result from non-combustion-related sources, principally from evaporation of various hydrocarbon fluids. This relationship is due to the fact that complete combustion of hydrocarbons is necessary to achieve high combustion efficiency. Three of the major combustion-related sources, then, involve processes wherein energy conversion is not the primary objective (carbon black production, ammonia production, and fluid catalytic cracking). The other two major combustion-related sources of hydrocarbon emissions (stationary internal combustion engines and steam boilers) do represent processes where energy conversion is the prime objective and they are relatively efficient combustion

processes (i.e., low hydrocarbon emission factors). They appear as major contributors only because of the massive quantities of hydrocarbon fuels that are burned in these systems.

SECTION 3

OTHER COMMENTS

Two other comments are of interest here, both involving uncertainties in the data presented in the published reports (1-3). One is related to the magnitude of, and the proportions between, the consumption of coal, oil, and natural gas in utility and industrial boilers. The other concerns the large uncertainties in the emissions from the large numbers of stationary internal combustion engines that are individually too small to be classified as point sources.

The major environmental, availability, and cost perturbations which have been affecting fuels for utility and industrial boilers are well-known. Initial trends toward lower cost, easily handled natural gas prior to 1970 were accelerated in the early 1970s as a result of environmental considerations. Then in the mid-1970s the lack of availability of natural gas sharply reversed this trend. Today, strong efforts are being made to decrease total fuel consumption, to increase the use of coal, and to eliminate natural gas in these applications. As a result, predictions of the magnitudes and relative proportions of the use of fossil-fuels in utility and industrial boilers are very uncertain.

Figure 7 graphically shows the problem, as exemplified by three attempts to predict trends in natural gas consumption in industrial and utility boilers. Past history, in this case, is no guide because gas consumption in these boilers has been increasing continuously for many decades and very strongly in the recent past. Neither are data on new boilers sales or boilers in fabrication good guides because boilers are being converted to oil- or coal-firing and, where conversion is not possible, some natural gas-fired boilers are being shut down entirely.

In the first attempt to project natural gas usage rates in utility and industrial boilers, in 1974, the trend to reduce natural gas usage in utility boilers was just becoming apparent. As a result, the best estimate trend was established to show some reduction, with an increased uncertainty range about that projection. Before that estimate was published, further public statements were made which appeared to indicate forthcoming

regulations that would even more severely reduce natural gas usage, and the original projected decreasing trend was steepened even further. Recent review of those data and projections, particularly in the light of new data and analyses published in 1978 by the Federal Energy Administration (4), resulted in the first data update, shown in Figure 7. That study has indicated that the reversal of the usage trend expected in the 1974-1975 period has not been as sharp as expected and the trend projected for the near future appears to be between those developed in the first two attempts. The negative slope in this updated trend is entirely due to projected decreases in natural gas usage in utility boilers while a small increase (2.1 percent per year) in usage in industrial boilers is projected.

Clearly, as a result of rapidly changing compromises between energy, environmental, economic, and political constraints, projection of fossil-fuel usage in utility and industrial boilers, in total magnitude of the heat input or in the split between the three major fuels, is very uncertain. As a result, emissions of the four air pollutants are similarly uncertain. For example, NO_x emissions from steam boilers projected to 1980 are considered uncertain within ±15 percent.

Another area of significant uncertainty involves the huge numbers of stationary internal combustion engines individually too small to qualify as point sources. Previous studies (5-6) have shown, for example, that well over one million gasoline-powered internal combustion engines were shipped from manufacturers every year for at least the last 10 years for uses ranging from small power tools to 1000 horsepower and greater compressors, pumps, and electrical power installations. Little data are available, however, on the actual applications of these engines, their average useful life, or their usage rates. Under one set of assumptions, NO_x and CO annual emissions from these small stationary internal combustion engines were estimated at about 9 and 14 million tons, respectively, in the year 1980; but these estimates could easily be low by factors of two or three. Thus, this category could be the largest single stationary source of both NO_x and CO. The NEDB data identify less than 2 and 6 million tons of NO_x and CO, respectively, in the total area source category, but the NEDB system of data collection could also have missed these large numbers of small engines. Since the subject inventory was limited to stationary point sources, no further effort was made to investigate this category. Efforts to trace at least the larger of these engines to the user and to estimate numbers of operating engines and their duty cycles certainly appear warranted.

REFERENCES

(1) O. W. Dykema and V. E. Kemp, Inventory of Combustion-Related Emissions from Stationary Sources, EPA-600/7-76-013, The Aerospace Corporation, El Segundo, California, (September 1976).

(2) O. W. Dykema and V. E. Kemp, Inventory of Combustion-Related Emissions from Stationary Sources (First Update), EPA-600/2-77-066a, The Aerospace Corporation, El Segundo, California (March 1977).

(3) V. E. Kemp and O. W. Dykema, Inventory of Combustion-Related Emissions from Stationary Sources (Second Update) , The Aerospace Corporation, El Segundo, California, (to be published as an EPA Report).

(4) Federal Energy Administration, National Energy Outlook, FEA-N-75/713 (1976).

(5) W. V. Roessler, et al, Assessment of the Applicability of Automotive Emission Control Technology to Stationary Engines, EPA-650/2-74-051, The Aerospace Corporation, El Segundo, California (July 1974).

(6) C. R. Metlowin, Stationary Internal Combustion Engines in the United States, EPA-R2-73-210, The Shell Development Company, Houston, Texas, (April 1973).

TABLE 1. SCOPE OF INVENTORY

Source	Emissions, million tons/year			
	NO_x	HC	CO	Part
Grand Total of Nationwide Emissions, All Sources[1]	21.62	23.79	111.16	28.81
	Emissions, % of Grand Total			
Mobile (transportation)[1]	42.4	56.3	64.9	5.3
Stationary Area Sources[1]	8.6	13.2	5.2	11.2
Stationary Point Sources[2]	48.9	30.0	29.9	83.5
Totals	100.0	100.0	100.0	100.0

Notes: (1) National Emissions Data System (NEDS) Data
(2) Subject of this Inventory

TABLE II. STATIONARY POINT SOURCE CRITERIA POLLUTANT EMISSIONS INVENTORY

Source Category	No. of Sources	PM_{10} Emissions (TPY)	SO_2 Emissions (TPY)	NO_x Emissions (TPY)	VOC Emissions (TPY)	CO Emissions (TPY)	Pb Emissions (TPY)
Boiler	12	45.2	12.8	38.5	2.1	18.4	0.03
Incinerator	4	3.1	0.9	6.2	0.4	2.7	0.01
Refinery Unit	11	22.6	8.4	19.3	1.8	9.5	0.02
Power Plant	6	31.0	14.2	27.6	0.9	11.3	0.04
Chemical Plant	9	18.7	6.1	15.4	3.6	7.2	0.01
Petroleum Coke Kiln	5	27.4	9.3	24.1	1.2	10.6	0.03
Natural Gas Processing	7	14.9	5.7	12.8	2.4	6.1	0.02
Petroleum Refinery	3	9.8	3.2	8.1	0.7	3.4	0.01
Other	1	2.3	0.6	1.9	0.2	0.8	0.00

TABLE III. MAJOR COMBUSTION PROCESSES CONTRIBUTING TO NO_x AND PARTICULATE EMISSIONS FROM STATIONARY POINT SOURCES

Emissions, % of 1976
Stationary Point Sources

	NO_x		Particulates	
	1976	1981	1976	1981
1. Steam boilers	84.4	80.8	46.6	48.8
2. Industries			32.9	34.7
a. Utility boilers	72.4	65.8	38.7	33.3
b. Industrial boilers	12.0	15.0	46.6	48.8
Total	84.4	80.8		
3. Fuels			42.8	46.6
a. Bituminous coal	62.1	74.6	2.3	3.1
b. Oil	12.1	3.7	0.4	0.7
c. Natural gas	10.2	2.5		
d. Other			46.6	48.8
Total	84.4	80.8		

EXAMPLE MODIFIED SOURCE CLASSIFICATION
CODE = 101002021

100000000 = EXTERNAL COMBUSTION, BOILERS
101000000 = ELECTRIC GENERATION
101002000 = BITUMINOUS COAL
101002020 = >100 mm Btu/hr PULVERIZED, DRY
101002021 = TANGENTIAL FIRING

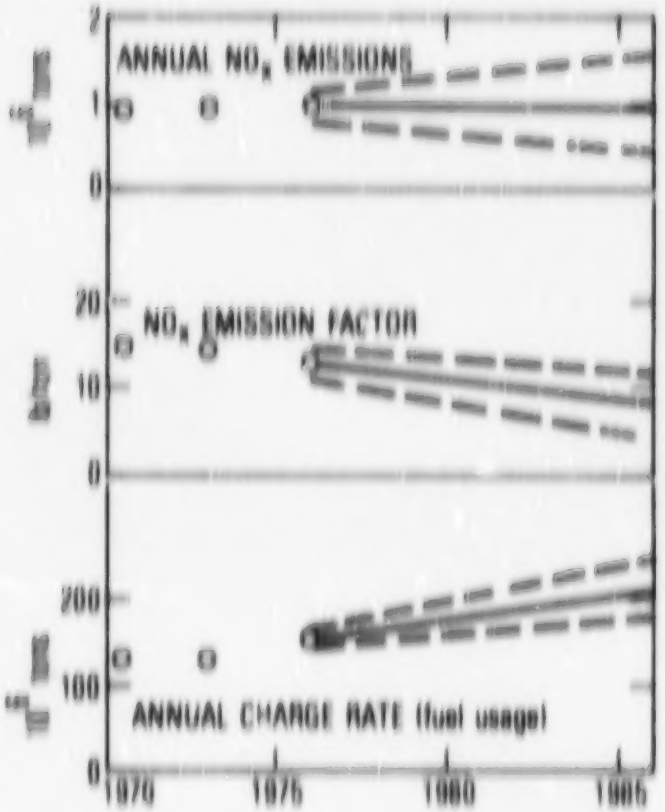

Figure 1. Example of the projections of best estimates and uncertainties.

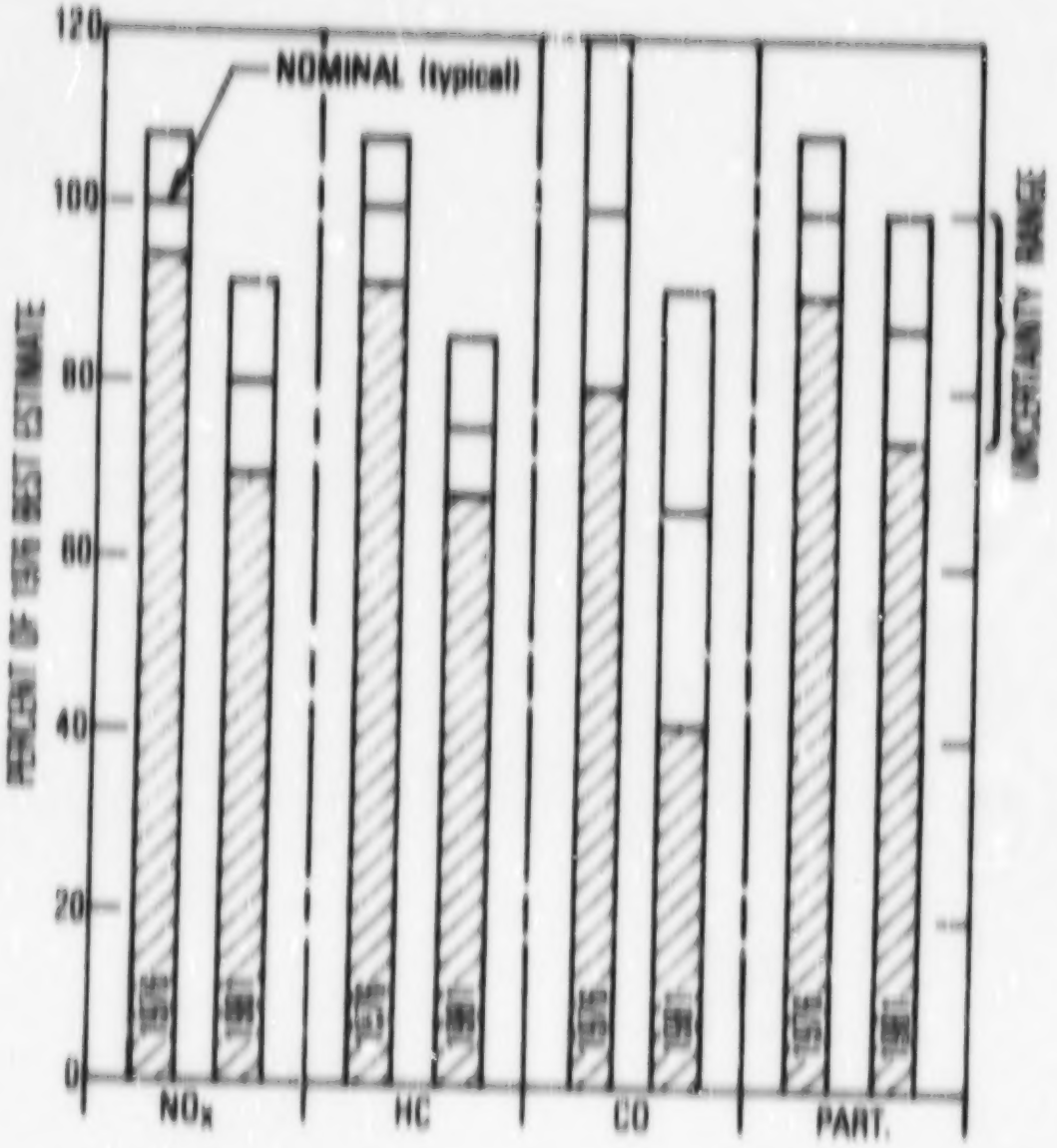

Figure 8. Projected trends in the four air pollutants from Stationary Point Sources.

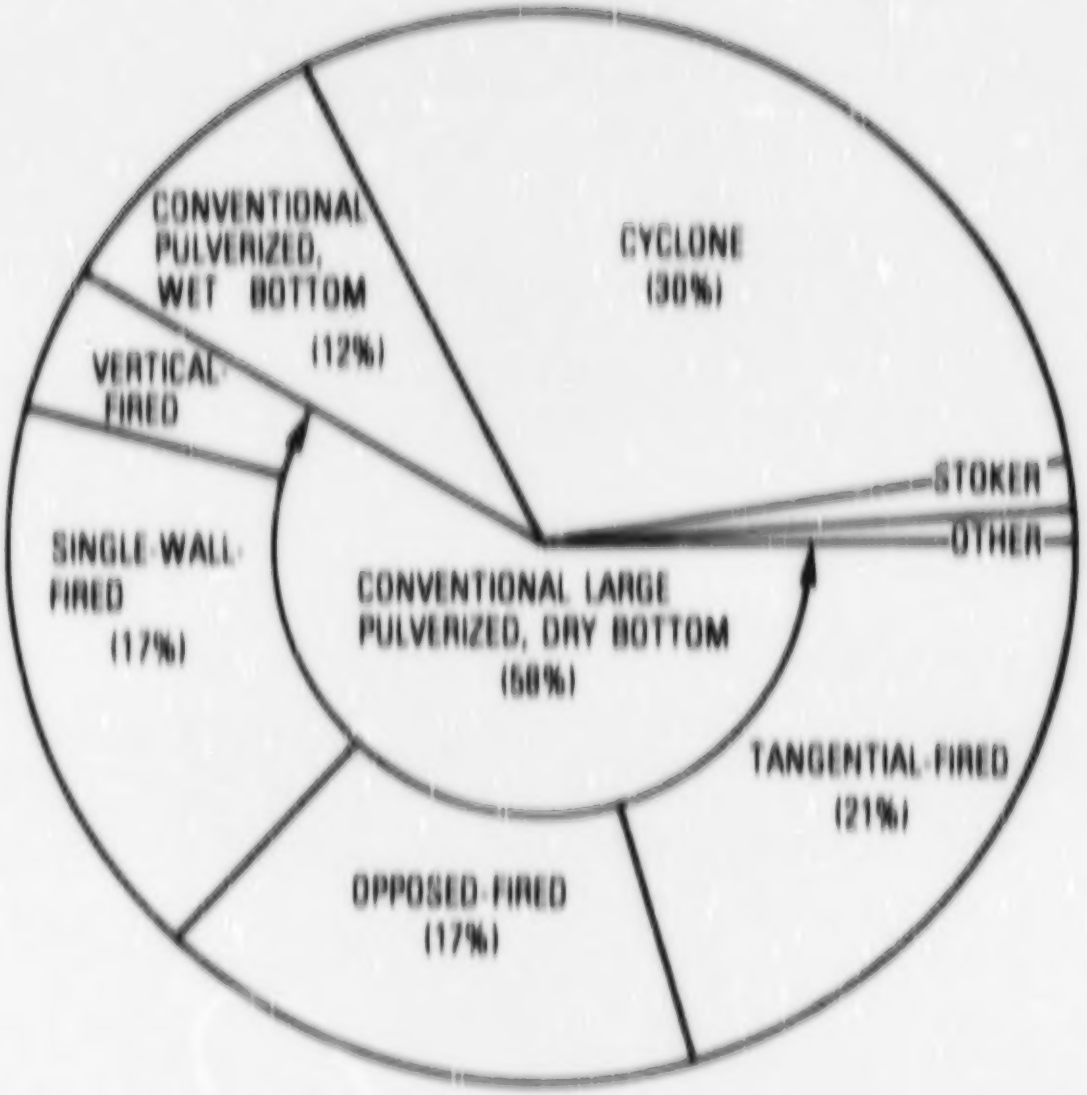

Figure 8. Projected NO_x emissions (4.6 million tons) from utility boilers firing bituminous coal in the year 1981.

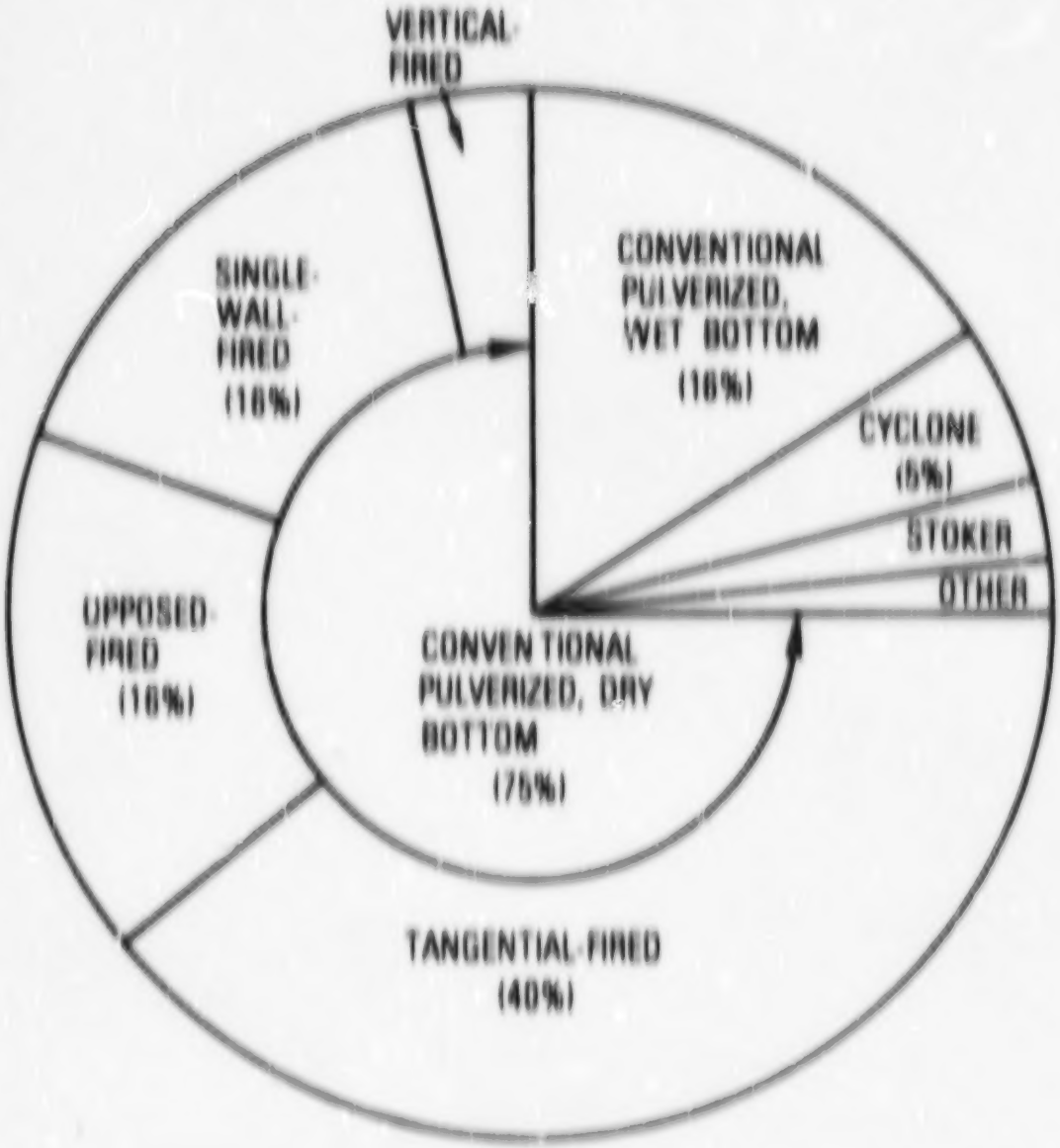

Figure 4. Projected particulate emissions (3.0 million tons) from utility boilers firing bituminous coal in the year 1981.

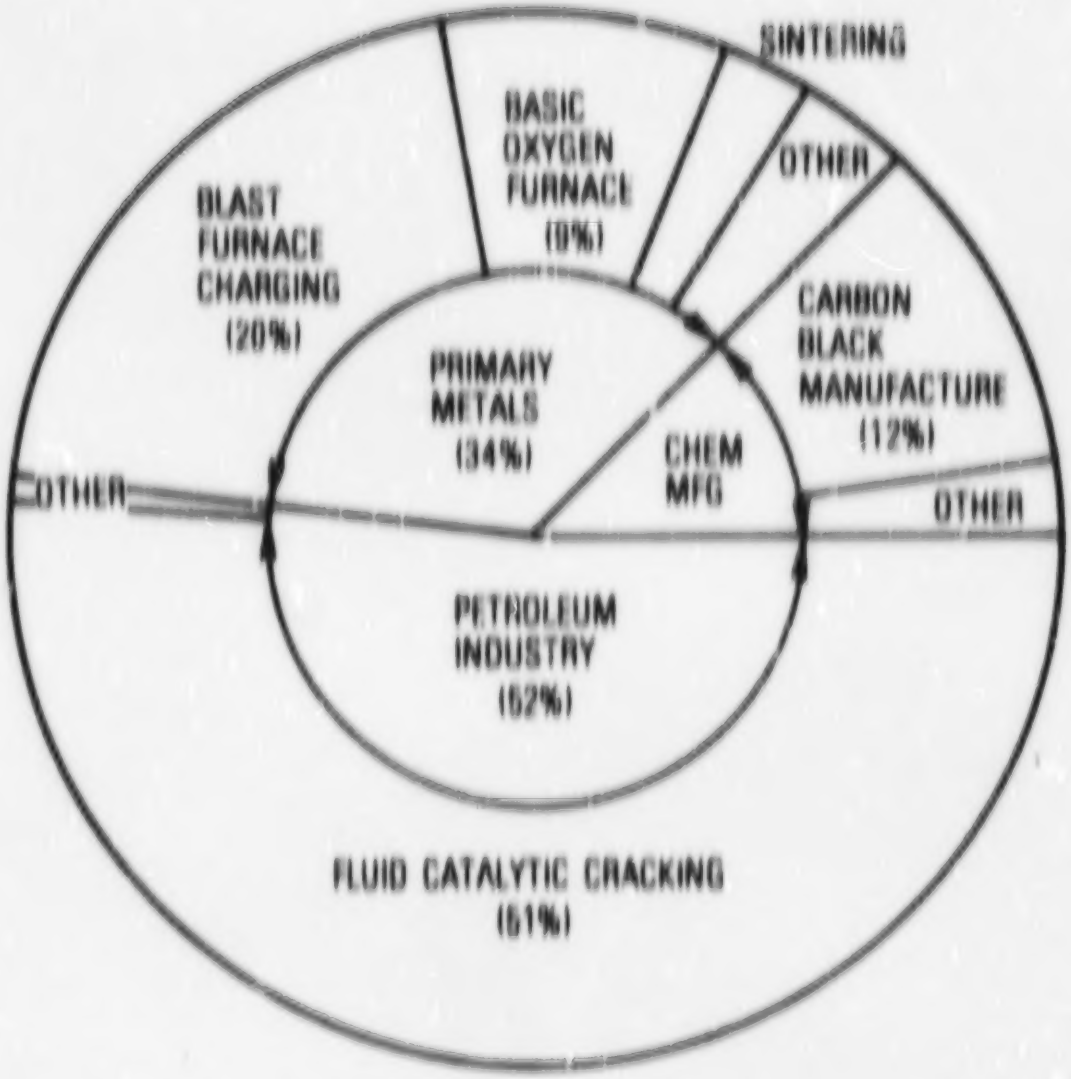

Figure 5. Projected CO emissions (19.8 million tons) from combustion-related stationary point sources in the year 1981.

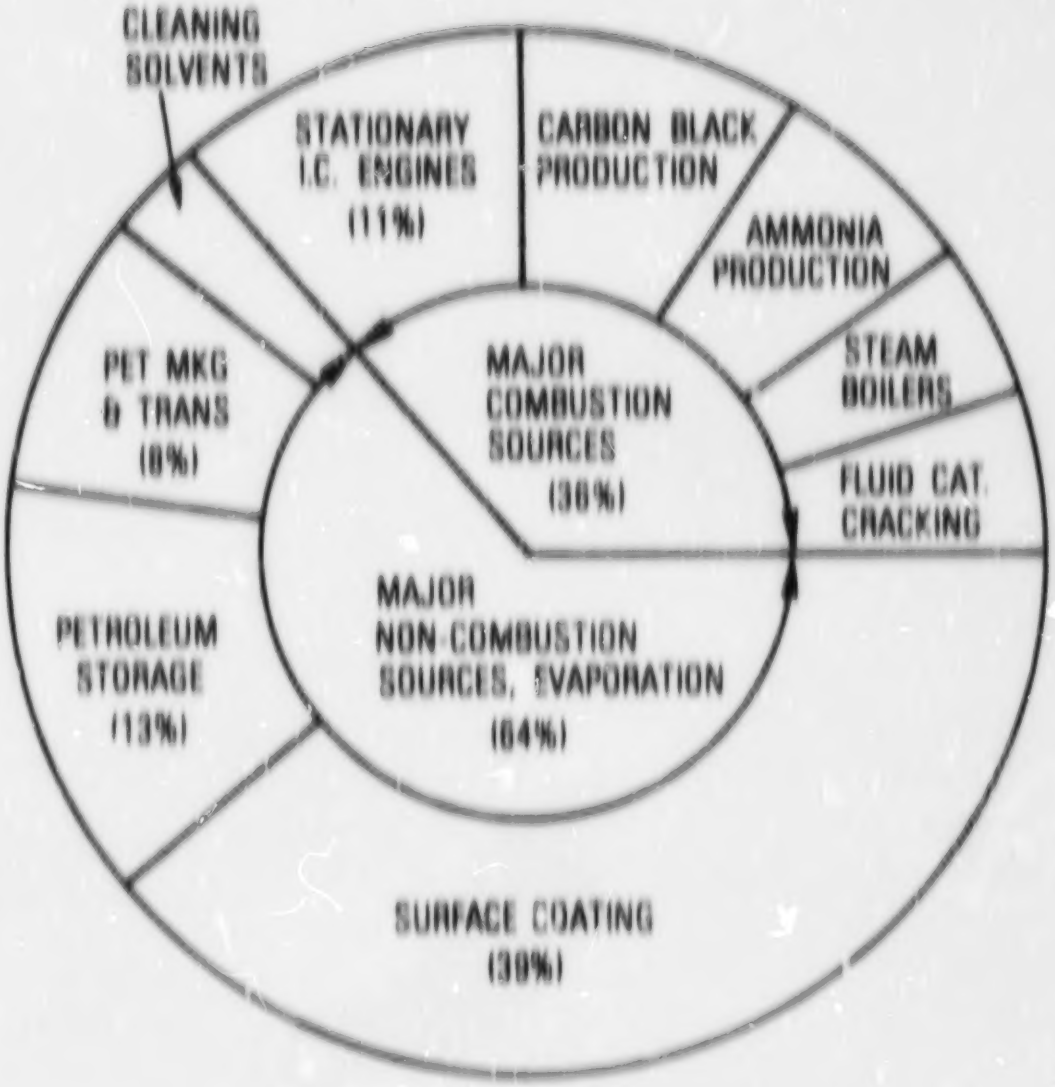

Figure 6. Projected hydrocarbon emissions (9.8 million tons) from major stationary point sources in the year 1981.

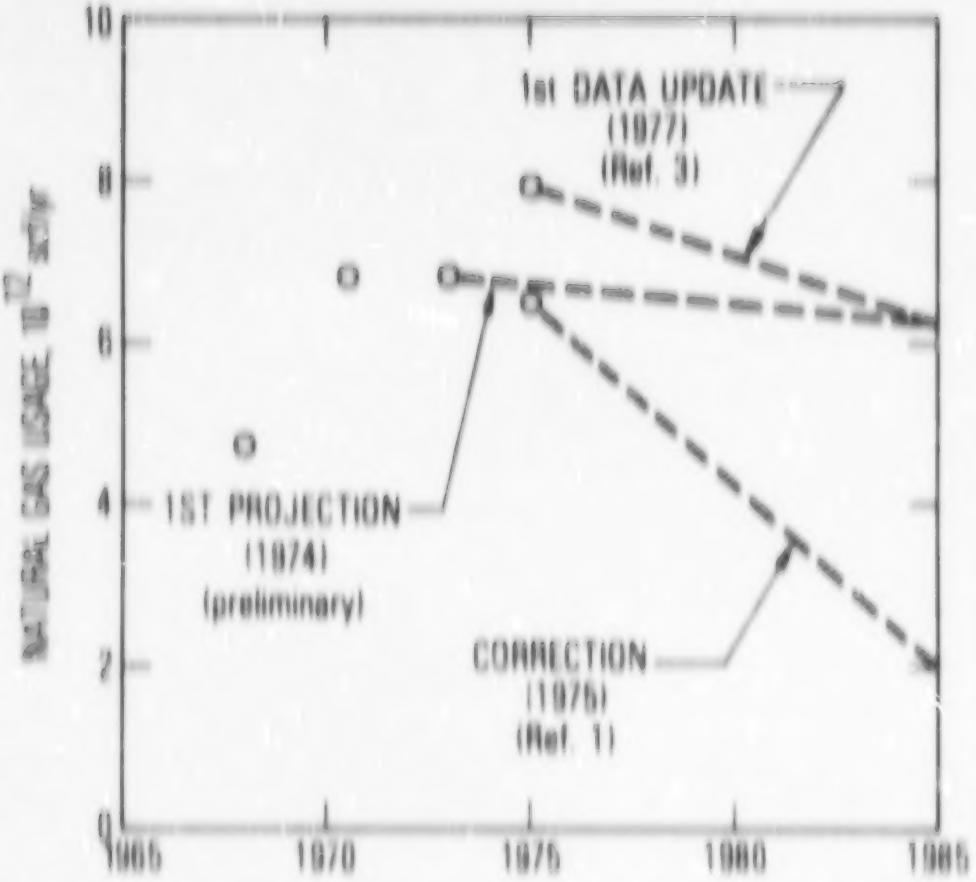

Figure 7. Natural gas usage rate projections for utility and industrial boilers.

EMISSIONS ASSESSMENT OF CONVENTIONAL COMBUSTION SYSTEMS

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ABSTRACT

The Industrial Environmental Research Laboratory (IERL) of the Environmental Protection Agency, in association with TRW Environmental Engineering Division, is conducting an extensive multimedia assessment of emissions from conventional stationary combustion systems. The program's purpose is the assessment of air, water, and solid waste emissions from approximately 51 categories of Residential, Commercial, Industrial and Utility combustion sources, burning gas, oil, coal and refuse. This involves the collection of existing test data plus an extensive sampling and analysis program. The forty-four (44) month program is scheduled for completion in the spring of 1980. Reports on specific types of combustion sources will be issued periodically starting in late 1977.

This study, Contract No. 68-02-2197, is being conducted by TRW Environmental Engineering Division under sponsorship of the United States Environmental Protection Agency.

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EMISSIONS ASSESSMENT OF CONVENTIONAL COMBUSTION SYSTEMS

INTRODUCTION

The Industrial Environmental Research Laboratory (IERL) of the Environmental Protection Agency, in association with TRW Environmental Engineering Division, is conducting an extensive emission assessment of stationary combustion systems. The program's purpose is the assessment of air, water and solid waste emissions from approximately 51 categories of Residential, Commercial, Industrial and Utility combustion sources. This involves the collection of existing test data plus an extensive sampling and analysis program. The forty-four (44) month program, directed by Dr. Ronald Venezia of IERL, is scheduled for completion in the spring of 1980. Reports on specific types of combustion sources will be issued periodically starting late 1977.

PROGRAM DESCRIPTION

TRW Environmental Engineering Division of Redondo Beach, California and its subcontractors, GCA/Technology Division of Bedford, Massachusetts and Engineering Sciences Incorporated of Arcadia, California are conducting an extensive multimedia assessment of emissions from stationary combustion systems. The combustion device categories being considered are shown in Table I. They are classified in terms of application and fuel type. The four (4) application categories are Residential, Commercial/Institutional, Industrial, and Electricity Generation. The seven (7) fuel categories are gas, distillate

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oil, residual oil, lignite coal, bituminous coal, anthracite coal, and refuse.

The major program goal is to provide an accurate and complete emissions data base for conventional combustion sources. To achieve this, existing data are being collected and analyzed for accuracy and adequacy. Using as a basis the adequacy of existing data, a test plan, which is subject to periodic revision, was developed. The purpose of the test plan is to identify those tests which will supply information currently missing from the existing data base and to collect additional information in areas where the existing data are questionable.

The sampling and analysis phase of this program is being conducted jointly by TRW and GCA. Tests are being conducted throughout the country at facilities provided on a voluntary basis by their owner/operator. Some analysis will be conducted in the field but the bulk of the analytical work will be done at TRW's and GCA's laboratory facilities at Redondo Beach, California and Bedford, Massachusetts, respectively.

EXISTING DATA

An extensive search for existing emission data was conducted. Data quality was evaluated in terms of criteria developed as part of this program. To be acceptable, the test data had to meet the following six (6) criteria:

- Only actual test data were acceptable. Emission estimates based on emission factors or engineering estimates were not acceptable. (This criteria eliminated data bases such as the National Emissions Data System (NEDS).)
- The combustion device had to be described adequately (i.e., design heat rate, type of burners, type of draft, etc.)
- The operating mode had to be defined adequately (i.e. load during the test).
- The design and operation of emission control devices had to be specified.

- A fuel analysis was required, with a minimum of trace elements, sulphur, and ash specified.
- The sampling and analysis methods had to be approved EPA, ASTM, or API methods.

The resulting data base was examined and those areas with insufficient data were identified. For most combustion source categories and pollutants, the existing data are not adequate.

The data gathering task is continuing throughout the program. As data become available from other sources, they will be included in the data base. TRW is working in cooperation with the following companies to collect additional test data for this program:

- Radian Corporation
- Hittman Associates
- Tennessee Valley Authority (TVA)
- Arthur D. Little
- Monsanto Research Corporation (MRC)
- Aerotherm/Acurex
- Battelle Corporation

TEST PLAN

A test plan was developed which calls for data collection in those areas where existing data are currently inadequate. In addition, projected changes in fuel use patterns and expected changes in the types of combustion equipment were considered. For example, because the use of anthracite coal is declining, fewer tests were scheduled on anthracite fired boilers than those burning other types of coal. Similarly, since the use of stoker fired units in the electric utility industry is declining, proportionally fewer tests were scheduled on this type of unit.

The test plan will be revised periodically. Currently about one-third of the available test dates have been left unscheduled. As data from this and other programs become available, the remaining tests will be assigned as appropriate. The purposes of the test plan are to maximize the amount of data collected with the resources available and to collect those data that will be most useful in future years.

SAMPLING AND ANALYSIS

A two tier approach to sampling and analysis is being used. At approximately 170 test sites a series of methodologies designated Level I procedures are being employed. Level I results are, when compared to most existing test data, quite detailed and sophisticated. The procedures are, however, not the most sophisticated available. Level I tests are designed to provide large amounts of data in a cost-effective manner. For example, stack gas measurements are being made at a single representative sampling point under semi-isokinetic conditions instead of using multipoint sampling under true isokinetic conditions. Similarly, the analysis of trace elements is being done with spark source mass spectrometry (SSMS) which is generally considered to be semiquantitative.

Data from the Level I tests and other test programs will be used to determine which sites are to be tested using the more sophisticated Level II procedures. State-of-the-Art Level II procedures provide more precise and detailed information on the composition and quantity of emissions. They consist of the most sophisticated sampling and analysis procedures available. Both the sampling and analysis, however, are more time consuming and expensive. For this reason, Level II sampling and analysis will be applied to approximately 21 sites.

The sampling and analysis procedures for flue gas are centered around the Source Assessment Sampling System (SASS). The SASS train, which was developed by Aerotherm/Accuren, is shown schematically in Figure 1. Cyclones collect particulates in three (3) size ranges: $10+\mu$, 3 to 10μ, and 1 to 3μ. A filter downstream of the cyclones collects any material that passes through

the cyclones. A condenser containing a bed of molecular sieve material follows. Water is condensed out and organic and inorganic material are trapped. A series of impingers complete the train. The impingers collect the most volatile organic and inorganic (such as mercury) compounds.

In addition to the six (6) SASS trains that are available for sampling stack emissions, a variety of other sampling equipment is available for taking samples of liquid effluents and solid wastes. Each will be used as circumstances dictate.

Three smaller vans and a trailer are available to support the two (2) 29-foot Mobile Environmental Assessment Laboratories that TRW designed and outfitted for this program (Figures 2, 3 and 4). Each mobile lab is equipped to provide lab and field facilities for the test crews. Each is equipped with 13 kilowatts of onboard power; potable and high purity water systems; a laminar flow hood; gas chromatographs; a refrigerator; an ice making machine; and a broad range of analytical instrumentation and supplies. There are also storage facilities for the SASS train and other sampling equipment.

On-board equipment will be used to analyze C_1 through C_6 organics, CO, SO_2 and NO_2. Samples for the other analyses will be prepared and shipped to the laboratory facilities in Redondo Beach and Bedford.

Figures 5, 6 and 7 show the basic analysis schemes for air emissions, water effluents and solid wastes, respectively. Table II summarizes the analyses that will be conducted.

Samples will be analyzed using a variety of instrumental and wet-chemical analysis methods including spark source mass spectrometry (SSMS), gas chromatography, gas chromatography/mass spectrometry (GC/MS), atomic absorption (AA), liquid chromatography, and infrared spectroscopy (IR).

After each particulate size range has been weighed separately, they are combined to give two samples -- particles that are smaller than 3μ and those that are larger than 3μ. Organics are removed by extraction and, sample size permitting, separated further into eight (8) classes of compounds.

each class is analyzed by infrared (IR) and mass spectrometric (MS) techniques. The remaining particulate is subjected to elemental analysis and analysis for sulfate ($SO_4^=$). Portions of the particulate samples will be stored as received for bioassay and particulate morphology studies. Currently these studies are under consideration.

The substances that pass through the front part of the train as gases are trapped either in the condenser condensate, the molecular sieve adsorbant, or the impingers. The samples collected at each of these locations are analyzed for organics and inorganics. The adsorbant is analyzed specifically for PCB's and POM's. The organic fractions are separated into eight (8) classes and analyzed in the manner described above.

The solid and liquid portions of liquid and slurry effluents are analyzed separately. The solids are subjected to the solid waste protocol; the liquids are analyzed in a manner similar to the SASS train condensate. The organic portions of each are separated into eight (8) classes for IR and MS analysis. In addition, a variety of water quality parameters such as pH, conductivity, chemical oxygen demand (COD), and biochemical oxygen demand (BOD), are measured.

Solid wastes are separated into water soluble and insoluble components. The organics are separated into volatile and non-volatile components and analyzed separately. The non-volatile components are separated into eight (8) classes and analyzed seperately.

The general plan is: all solid, liquid and gas samples, regardless of the form in which they were originally emitted, will be analyzed for volatile and non-volatile organic and inorganic components. It is recognized, however, that it will not be feasible nor reasonable to conduct all tests on all samples. For example, particulate emissions from gas fired units are very low. It is impractical to collect a large enough particulate sample to conduct all of the organic and inorganic analyses. Furthermore, since gas fuel contains essentially no trace elements, it seems unreasonable to search for them in the flue gas.

QUALITY CONTROL

A comprehensive quality control function for both sampling and analysis is being conducted. The objectives of this part of the program are to establish and supervise procedures that assure reliable data. More specifically the objectives are:

- To establish acceptable limits on data quality;
- To establish procedures that ensure the quality of data from various sites and laboratories;
- To establish guidelines for the selection and use of site-specific measurement methods;
- To develop and implement quality control programs on each specific sampling technique and/or analysis;
- To identify areas requiring new or improved measurement methods.

SUMMARY

The combustion emissions assessment program will provide detailed and accurate data on the air, water, and solid waste emissions from stationary combustion systems. The data being collected include particulate size distributions, trace element composition (including volatile elements), organic emissions and composition, and standard water quality parameters. These data will provide a sound basis for assessing the environmental impact of stationary combustion sources as well as a data base for other research programs.

TABLE I. COMBUSTION SOURCE CATEGORIES

Residential Ext Comb Anthracite
Residential Ext Comb Bituminous
Residential Ext Comb Dist Oil
Residential Ext Comb Gas
Residential Ext Comb Wood
Residential Ext Comb Lignite
Commercial/Institutional Ext Comb Resid Oil Other
Commercial/Institutional Ext Comb Resid Oil Tang Fire
Commercial/Institutional Int Comb Dist Oil
Commercial/Institutional Ext Comb Dist Oil Tang Fire
Commercial/Institutional Ext Comb Dist Oil Other
Commercial/Institutional Ext Comb Gas Other
Commercial/Institutional Int Comb Gas
Commercial/Institutional Ext Comb Gas Tang Fire
Commercial/Institutional Ext Comb Anthracite Stoker
Commercial/Institutional Ext Comb Bituminous Stoker
Commercial/Institutional Ext Comb Bituminous Pulv Dry Bottom
Commercial/Institutional Ext Comb Bituminous Pulv Wet Bottom
Industrial Ext Comb Resid Oil Other
Industrial Ext Comb Resid Oil Tang Fire
Industrial Ext Comb Bituminous Stoker
Industrial Ext Comb Bituminous Pulv Wet Bottom
Industrial Ext Comb Bituminous Cyclone
Industrial Ext Comb Gas Other
Industrial Int Comb Gas Recip'Eng
Industrial Int Comb Gas Turbine
Industrial Ext Comb Gas Tang Fire

List of Abbreviations:

Ext Comb - external combustion
Int Comb - internal combustion
Pulv - pulverized
Tang - tangential
Recip Eng - reciprocating engine

TABLE 1. COMBUSTION SOURCE CATEGORIES (CONT.)

Electricity Generation Ext Comb Bituminous Pulv Wet Bottom
Electricity Generation Ext Comb Bituminous Cyclone
Electricity Generation Ext Comb Bituminous Stoker
Electricity Generation Ext Comb Resid Oil Other
Electricity Generation Int Comb Dist Oil Turbine
Electricity Generation Int Comb Dist Oil Recip Eng
Electricity Generation Int Comb Gas Turbine
Electricity Generation Int Comb Gas Recip Eng
Electricity Generation Ext Comb Gas Other
Electricity Generation Ext Comb Gas Tang Fire
Electricity Generation Ext Comb Dist Oil Other
Electricity Generation Ext Comb Dist Oil Tang Fire
Electricity Generation Ext Comb Anthracite Stoker
Electricity Generation Ext Comb Anthracite Pulv Dry Bottom
Electricity Generation Ext Comb Lignite Pulv Dry Bottom
Electricity Generation Ext Comb Lignite Pulv Wet Bottom
Electricity Generation Ext Comb Lignite Cyclone
Electricity Generation Ext Comb Lignite Stoker
Electricity Generation Ext Comb Refuse

Industrial Int Comb Dist Oil Recip Eng
Industrial Ext Comb Oil Other
Industrial Int Comb Dist Oil Turbine
Industrial Ext Comb Dist Oil Tang Fire
Industrial Ext Comb Refuse
Industrial Ext Comb Anthracite Stoker
Industrial Ext Comb Lignite Stoker

TABLE II. SUMMARY OF ANALYSES TO BE PERFORMED

AIR	WATER	SOLIDS
Particulates, by size fractions	C_1-C_{12} Organics	Organics
HO_A	Greater than C_{12} organics by functional group	Trace Elements (seventy metals)
SO_A	PCB	Selected Anions (such as sulfates, nitrates, chlorides and fluorides)
C_1-C_{12} Organics	PCM	
Greater than C_{12} organics by functional group	Trace Elements (seventy metals)	Other Selected Parameters
PCB	Selected Anions (such as fluorides, chlorides, sulfates, nitrates, cyanide, and phosphates)	
PCM		
Trace Elements (seventy metals)	Nitrogen-Ammonia	
Selected Anions (such as fluorides, chlorides, and nitrates)	pH	
	Conductivity	
Other Selected Parameters	Total suspended particulates	
	Oil and Grease	
	Other Selected Parameters	

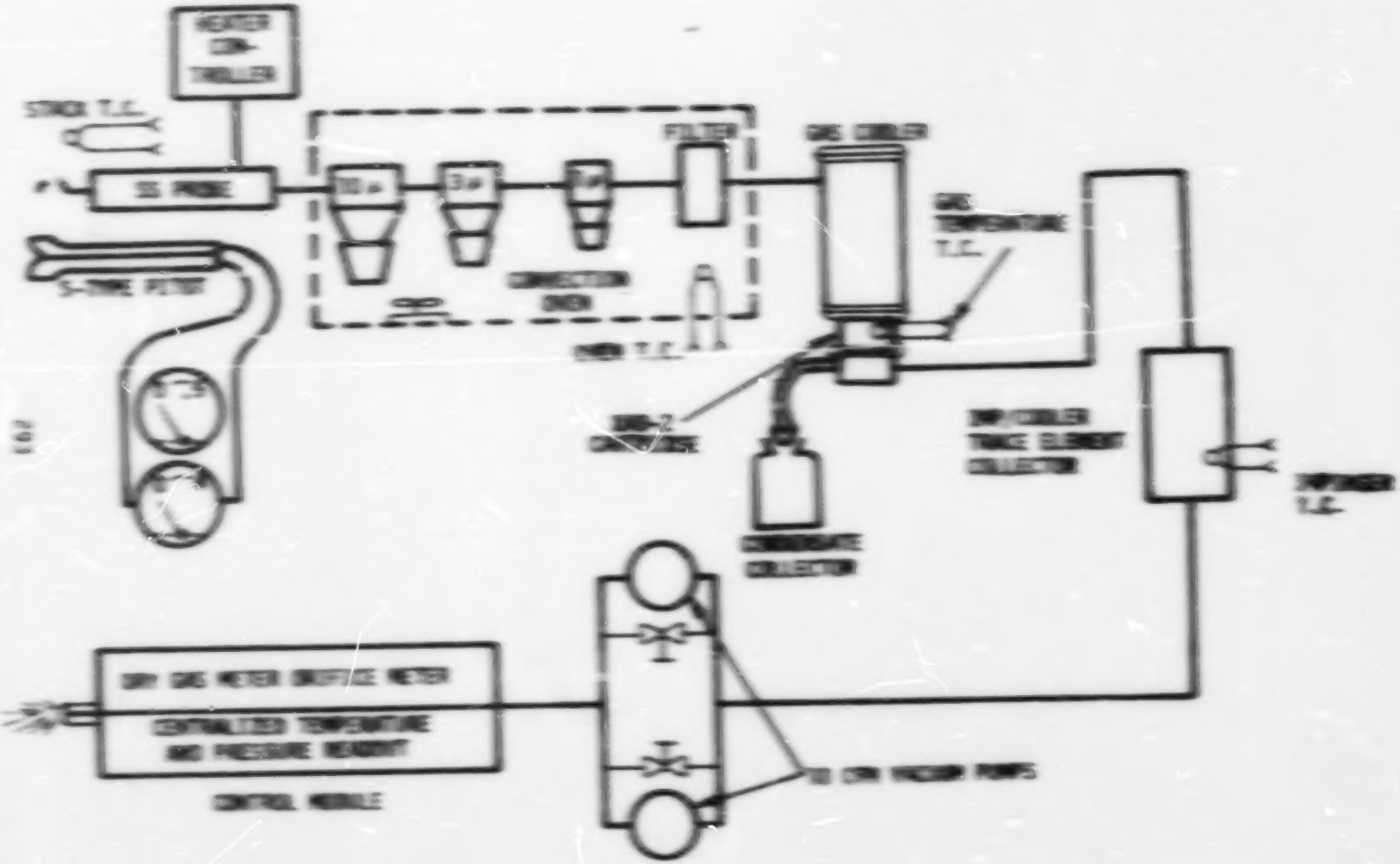

Figure 1. SKS Schematic

Figure 2. Mobile Environmental Assessment Laboratories

Figure 1. Water Environmental Research Laboratory

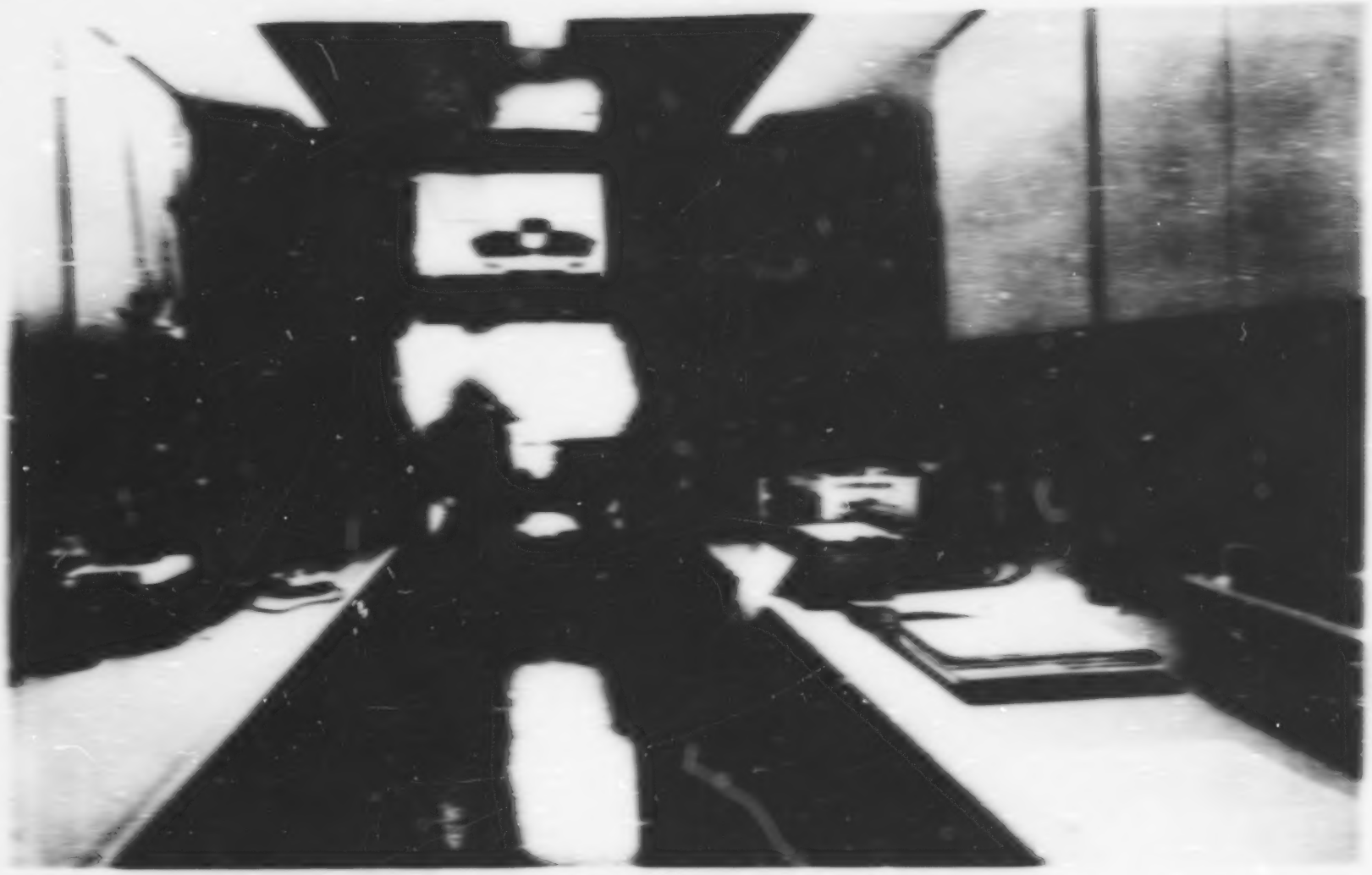

Figure 4. Mobile Environmental Assessment Laboratory

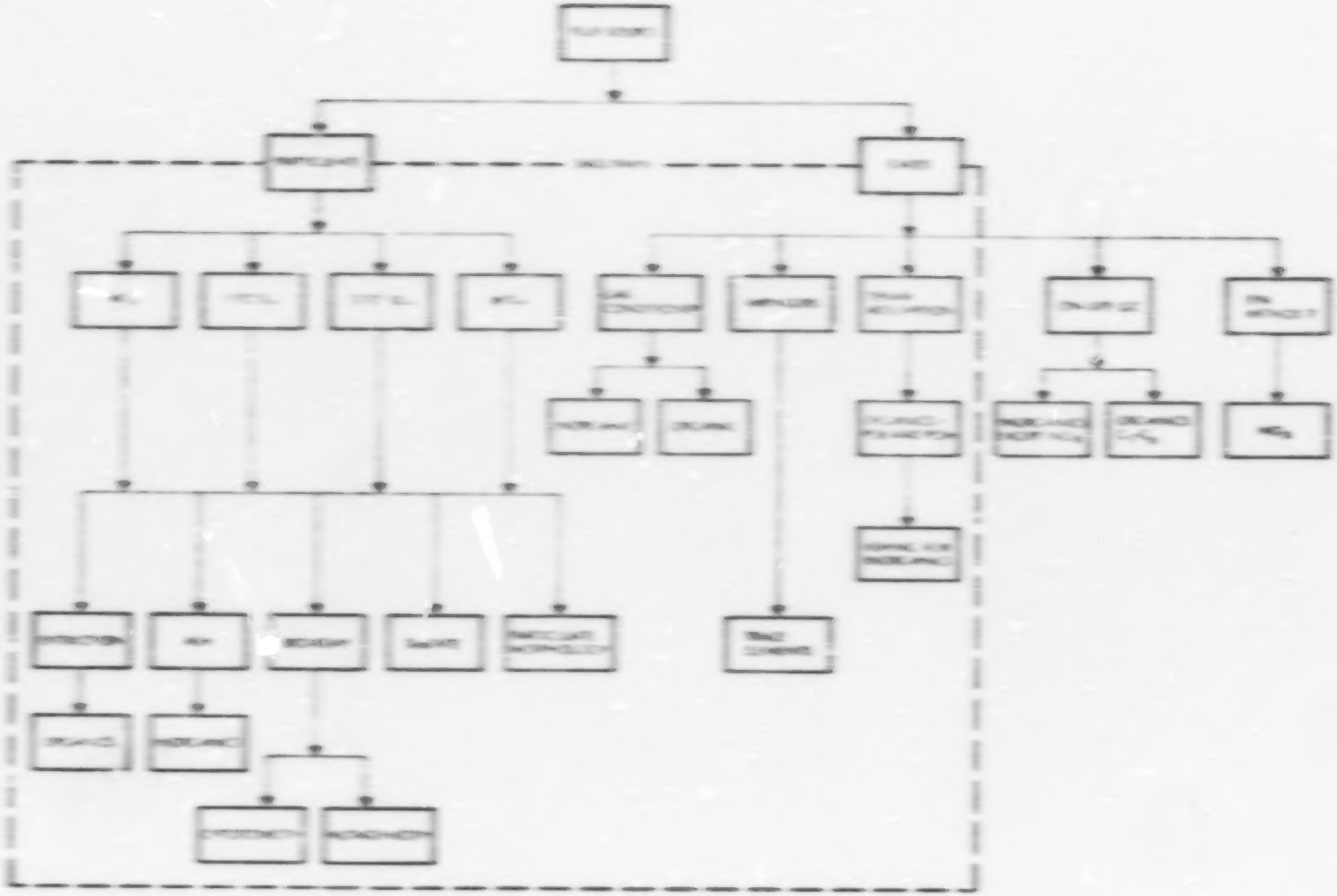

Figure 5. Analysis Scheme for Air Emissions

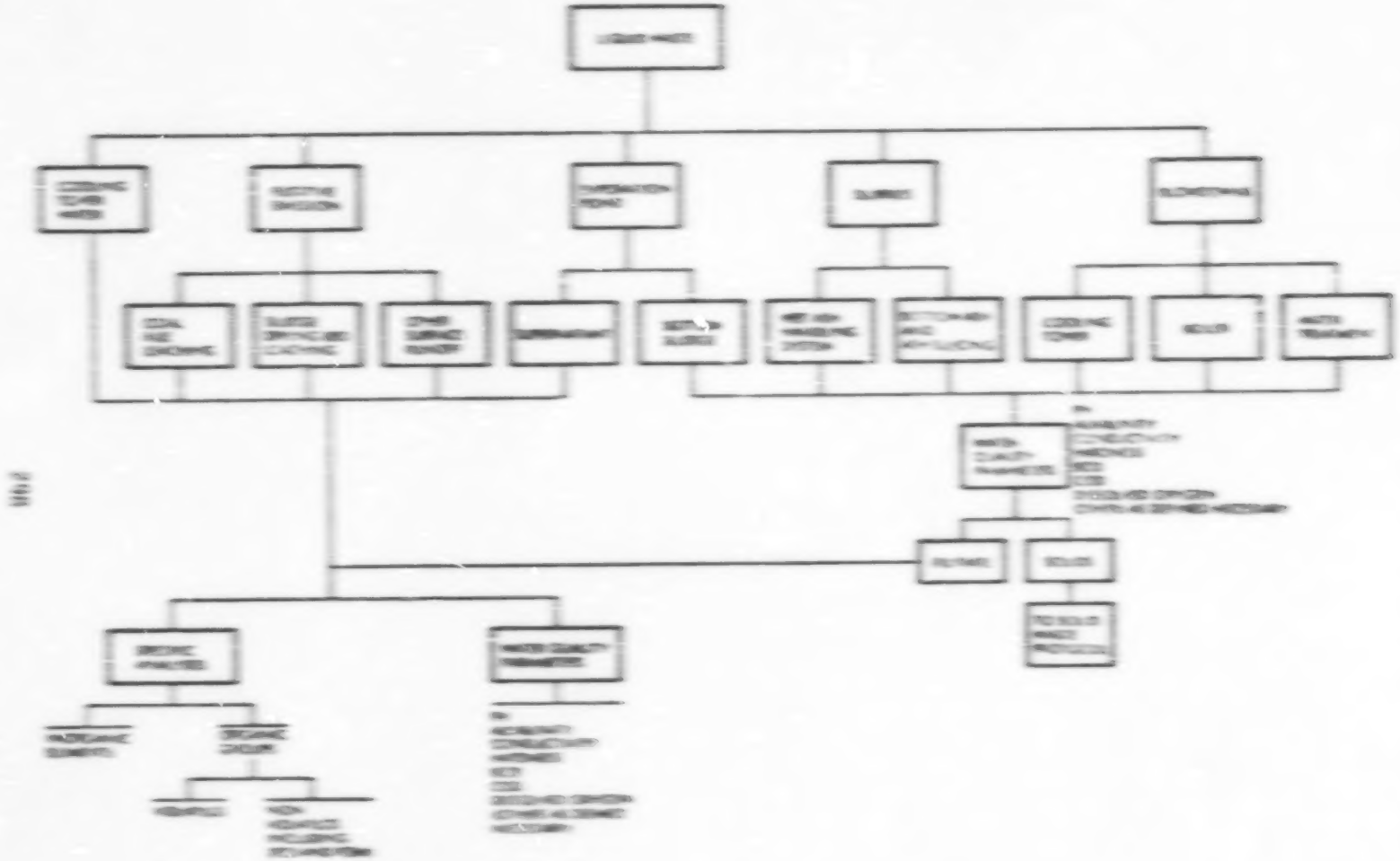

Figure 6. Analysis Scheme For Water Effluents

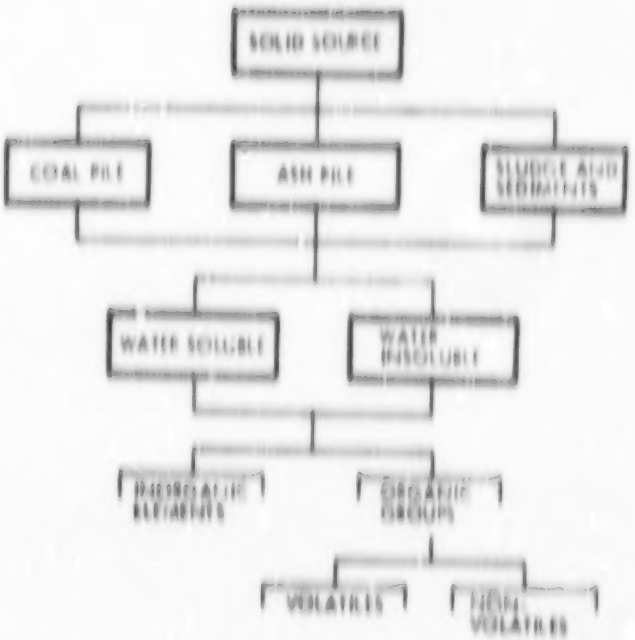

Figure 7. Analysis Scheme For Solid Waste

PANEL: COMBUSTION SOURCE/AIR POLLUTION REGULATIONS -- PRESENT AND PROJECTED

1 -- Federal Regulations
Jack R. Farmer

2 -- Regional Regulations
Robert Dupree

Panel discussion abstracts will be included in Volume V.

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